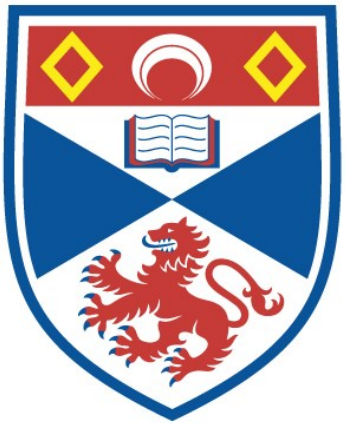
ASPECTS OF THE CHEMISTRY OF IRON-NITROSYLS

Andrew Richard Hyde

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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ASPECTS OF THE CHEMISTRY OF IRON - NITROSYLS.

A thesis presented for the degree of

DOCTOR OF PHILOSOPHY

in the University of St. Andrews

by

Andrew Richard Hyde, B.Sc.

September 1984.

To Rita

Declaration

I declare that this thesis is my own composition, that it is a record of my own work, and that it has not previously been submitted in application for a higher degree.

Andrew R. Hyde

September 1984

Certificate.

I hereby certify that Andrew Richard Hyde has spent twelve terms of research under my supervision, has fulfilled the conditions of Ordinance General No. 12 and Resolution of the University Court, 1967, No. 1, and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Dr. C. Glidewell

Research Supervisor

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Abstract.

The work described in this thesis is a study of iron-sulphur-nitrosyls and related compounds. Chapter One is an introduction to the work presented. Chapter Two is concerned with the analogous $Fe_2(SR)_2(CO)_6$ and its conversion to $Fe_2(SR)_2(NO)_4$. Chapter Three is concerned with an n.m.r. study of $Fe_2(SR)_2(NO)_4$, $Fe_4X_4(NO)_4$ and $[Fe_4X_3(NO)_7]^-$ (X=S,Se). Chapter Four is concerned with an e.p.r. examination of $Fe_2(SR)_2(NO)_4$ and bridging ligand exchange reactions. Chapter Five is concerned with a similar examination of $Fe_2I_2(NO)_4$. Chapter Six is concerned with an examination of ligand exchange processes in $Fe_4S_4(NO)_4$ and $[Fe_4S_3(NO)_7]^-$. Chapter Seven is concerned with an investigation of iron-sulphur protein models and their conversion to iron-nitrosyls.

CONTENTS.

CHAPTER ONE

INTRODUCTION

1.1 Iron-Chalcogen-Nitrosyls; Structure, Synthesis and Reactions.

In 1858, Roussin[1] demonstrated that addition of iron(II) sulphate to an aqueous mixture of ammonium sulphide and sodium nitrite yielded a black water soluble complex, $[Fe_4S_3(NO)_7]^-$. The crystal structure of this anion has been determined by both Johanson and Lipscomb[2] in the caesium salt and by Chu and Dahl[3](fig.1.1) in the tetraphenylarsonium salt. The complex consists of a trigonal pyramid of iron atoms, with triply-bridging sulphur atoms above three faces of the pyramid. The unique apical iron atom in the complex is coordinated to a single nitrosyl, three sulphur atoms and the three basal iron atoms. The three equivalent basal iron atoms are coordinated to two nitrosyl ligands, the apical iron and two bridging sulphur atoms. There are no direct bonds between the basal iron atoms.

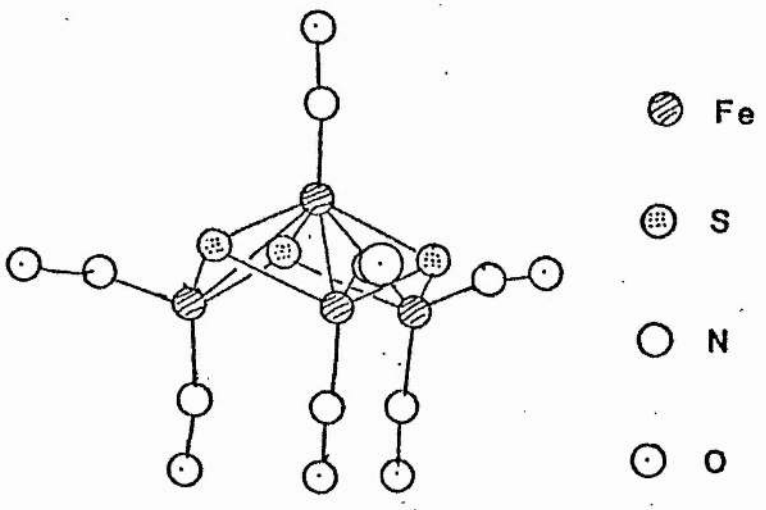


Fig. 1.1; Structure of Roussin's Black salt[3].

In addition to reporting the formation of salts of $[Fe_4S_3(NO)_7]^-$, Roussin's Black Salt(RBS), Roussin observed[1] that a red solution is generated by refluxing $[Fe_4S_3(NO)_7]^-$ in aqueous base. This complex has since been characterised as containing the dianion $[Fe_2S_2(NO)_4]^{-2}$, Roussin's Red Salt[4]. The crystal structure of this anion has recently been determined by Lin, Huang and Lu[4] and consists of a planar Fe_2S_2 ring (fig. 1.2). It has been found that the bridging sulphur atoms can be alkylated by the action of alkyl halides[5,6] to yield alkyl esters of the red salt $Fe_2(SR)_2(NO)_4$. The crystal structure of the ethyl ester, $Fe_2(SEt)_2(NO)_4$ has been determined[7] and is analogous to that obtained for $[Fe_2S_2(NO)_4]^{-2}$.

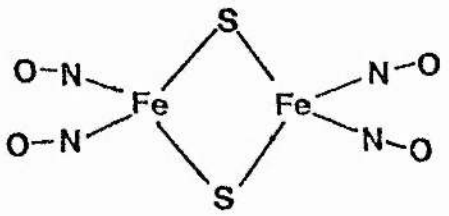


Fig. 1.2; Structure of Roussin's Red salt[4].

The mercury complex, $[Fe(CO)_3(NO)]_2Hg$ has been shown to react with elemental sulphur[8] to yield the cubane analogue, $Fe_4S_4(NO)_4$. X-ray structural analysis of the complex (fig.1.3) reveals it to be composed of a tetrahedron of iron atoms, with a triply-bridging sulphur atom above each of the four faces of the tetrahedron and with a single nitrosyl ligand terminally bound to each iron atom. Chu and Dahl[3] demonstrated by cyclic voltammetry that the cubane analogue

exhibits two reversible one electron oxidation/reduction waves to yield $[Fe_4S_4(NO)_4]^n$ (n=-1,0,+1). In an attempt to isolate the monoanion from $Fe_4S_4(NO)_4$ it was found that the resulting product was the monoanion $[Fe_4S_3(NO)_7]^-$ [3]. This reaction is an example of the interconvertibility of these iron-sulphur-nitrosyls.

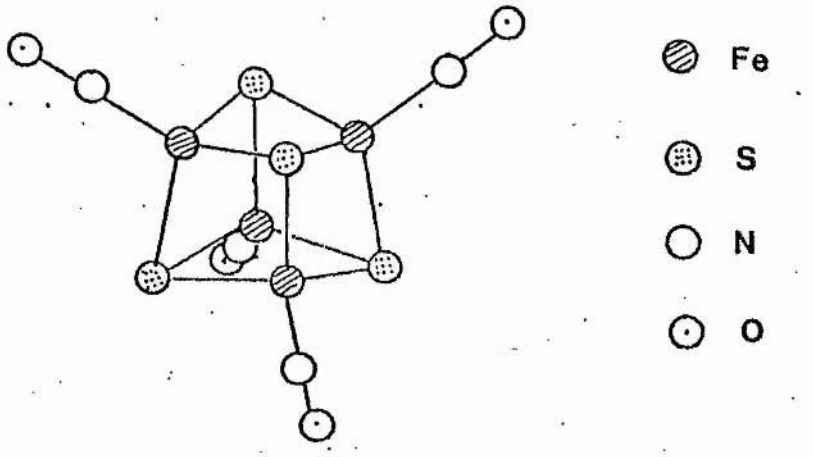


Fig. 1.3; Structure of the cubane analogue $Fe_4S_4(NO)_4$ [8].

Early studies on the complexes $[Fe_2S_2(NO)_4]^{-2}$, its alkyl analogues[9-15], and $[Fe_4S_3(NO)_7]^-$ [16-20] were mainly concerned with determining their structure and constitution; specifically to determine the oxidation state of the constituent iron atoms. Formal oxidation states can be ascribed to the constituent metal atoms if it is assumed that the sulphur is present as S^{-2} and that the nitrosyls are present as NO^+ (from the approximately linear Fe-N-O bonds[3]). Using these values, formal oxidation states of $+1(d^7)$ for the iron atoms in the cubane analogue $Fe_4S_4(NO)_4$ and $-1(d^9)$ for the iron atoms in both $[Fe_2S_2(NO)_4]^{-2}$ and $Fe_2(SR)_2(NO)_4$ can be assigned. If all of the iron atoms in $[Fe_4S_3(NO)_7]^-$ have the same oxidation state, then the resulting ascribed oxidation state is -1/2. If however the apical iron atom is assumed to be essentially identical to the $+1(d^7)$ iron atoms in $Fe_4S_4(NO)_4$ then the basal dinitrosylated iron atoms are

ascribed a formal oxidation state of $-1(d^9)$, the same as for iron in $Fe_2(SR)_2(NO)_4$ and $[Fe_2S_2(NO)_4]^{-2}$. Mössbauer examination of $[Fe_4S_3(NO)_7]^-$ by various workers has resulted in inconsistent results. A low temperature study[21] revealed a 3:1 ratio of two types of iron assumed to be $-1(d^7)$ and $+1(d^9)$ respectively which agrees with the formal oxidation states ascribed above. However, a more recent study[22] indicates that differentiation between the two different types of iron atom is not possible.

From the modern viewpoint, the argument over the oxidation states of the constituent atoms in these metal clusters is essentially irrelevant since bonding in these compounds is best considered in molecular orbital terms. Dahl and coworkers[23] have developed a qualitative cluster molecular orbital model for the Fe_4S_4 cubane analogues and have used an analogous description for the bonding in $[Fe_4S_3(NO)_7]^-$ [3]. This involves occupation of 17 out of 20 tetra iron cluster molecular orbitals, the 34 valence electrons coming from one apical d^7 iron atom and three basal d^9 iron atoms. Under a localised valence bond representation, this is equivalent to there being an electron-pair bond between the apical iron atom and each of the basal iron atoms. A more quantitative model has been developed for metal clusters by Hoffmann and coworkers[24,25]. This has been applied to the metal clusters $[Fe_4S_4(NO)_4]$, $[Fe_4S_3(NO)_7]^-$ together with $[Fe_2S_2(NO)_4]^{-2}$ and its acid, $Fe_2(SH)_2(NO)_4$ to obtain a more quantitative model of the bonding in these compounds[26].

Iron-chalcogen-nitrosyls have been shown to demonstrate many structural similarities. The cubane analogues $Fe_4S_4(NO)_4$ and $Fe_4Se_4(NO)_4$ have both been characterised by x-ray spectroscopy[8,27]. In both of these complexes the Fe_4X_4 cores demonstrate cubic T_d geometry, the major structural variation between the sulphur and selenium analogue being an increase in bond lengths which has been described as being primarily due to the increase in the size of the chalcogen atoms[27]. In addition to the structural characterisation of the neutral complexes, the monoanions $[Fe_4S_4(NO)_4]^-$ [28] and $[Fe_4Se_4(NO)_4]^-$ [27] have been isolated and characterised. Like the neutral complexes, the monoanions are essentially identical. The dianion $[Fe_4Se_4(NO)_4]^{-2}$ has been synthesised[27], though it has yet to be structurally characterised. Molecular orbital models[26] of the reduced complexes $[Fe_4S_4(NO)_4]^-$ and $[Fe_4S_3(NO)_7]^{-2}$ place the additional electrons into antibonding molecular orbitals within the tetrametal core. The resulting complexes are presumed to be less stable than the original complexes; this is demonstrated by the observed ready decomposition of the dianion; $[Fe_4Se_4(NO)_4]^{-2}$ [27].

In addition to the preparation of the μ_2-alkylthiolato complexes $Fe_2(SR)_2(NO)_4$ both selenium[28-30] and tellurium[27,30,31] analogues have been prepared. Crystal structures of both $Fe_2(SEt)_2(NO)_4$[7] and $Fe_2(TePh)_2(NO)_4$[27] have been reported, although as yet a crystal structure of a selenium analogue has not been recorded. The series of compounds $Fe_2B_2(NO)_4$ are all diamagnetic, this has been explained as being due to the existence of an Fe-Fe bond[32]. In the 'quantitative' molecular orbital examination[26] of both $[Fe_2S_2(NO)_4]^{-2}$ and

$Fe_2(SH)_2(NO)_4$ the iron atoms are regarded as Fe^{-1}, d^9: resulting in nine occupied molecular orbitals primarily concentrated on the iron atoms. Five of these are assigned bonding and four antibonding with respect to the iron-iron interaction, indicative of a net total of two bonding electrons. Comparison of the structures of the sulphur and tellurium complexes shows there to be a large deviation in the planar Fe_2B_2 (B=S[7], Te[27], I[32], P[33]) rhombus when the bridging atoms are changed from S to Te: ca. 74.0° to 67.2° for the Fe-S-Fe and Fe-Te-Fe angles respectively. This distortion of the Fe_2B_2 ring has been explained as resulting from a minimization in the increase in the Fe-Fe bond distance of 0.08Å (from 2.72Å to 2.80Å) relative to the increase in the Fe-B distance of 0.27Å (from 2.26Å to 2.53Å).

In addition to the μ_2-chalcogen analogues of $Fe_2X_2(NO)_4$ a number of other analogues are known, with bridging groups, I^- [32], Br^- [34], PR_2^- [33], and $AsMe_2^-$ [35]. The crystal structure of the μ_2-iodo complex $Fe_2I_2(NO)_4$ has been reported[32]; comparison of its structure with those of the chalcogen analogues $Fe_2(XR)_2(NO)_4$ yields noteworthy inconsistencies. Exchange of $PhTe^-$ for EtS^- results in a decrease in the Fe-B-Fe bond angle of 6.8°; this is notably larger than the 1.4° for the exchange of iodide for EtS^-. This is surprising since tellurium and iodine are more similar in size than sulphur and tellurium. Substitution of iodine for RS^- results in a Fe_2S_2 ring expansion which results in an increase in the Fe-Fe bond distance of 0.33Å (from 2.73Å to 3.05Å) resulting in a weaker Fe-Fe bond. The crystal structure of the complex $Fe_2(PMe_2)_2(NO)_4$ is known[33]. Comparison of its structure with that of its chalcogen and iodide analogues reveals the compound to be very similar to that of

$Fe_2(SEt)_2(NO)_4$ (Fe-B=2.22Å, Fe-Fe=2.71Å and Fe-B-Fe=75.4°). It appears therefore that the iodide analogue is a special case with its long iron-iron bond.

In addition to $[Fe_4S_3(NO)_7]^-$ the selenium analogue $[Fe_4Se_3(NO)_7]^-$ has been synthesised[36,37], although as yet it has not been characterised by x-ray crystallography. The synthesis of the selenium analogue is similar to that of the well-characterised sulphur complex. Reaction of PPh_3 with $Fe_4Se_4(NO)_4$ yields neutral $Fe_4Se_3(NO)_4(PPh_3)_3$[27] (fig. 1.4) which like $[Fe_4Se_3(NO)_7]^-$ contains a Fe_4X_3 core.

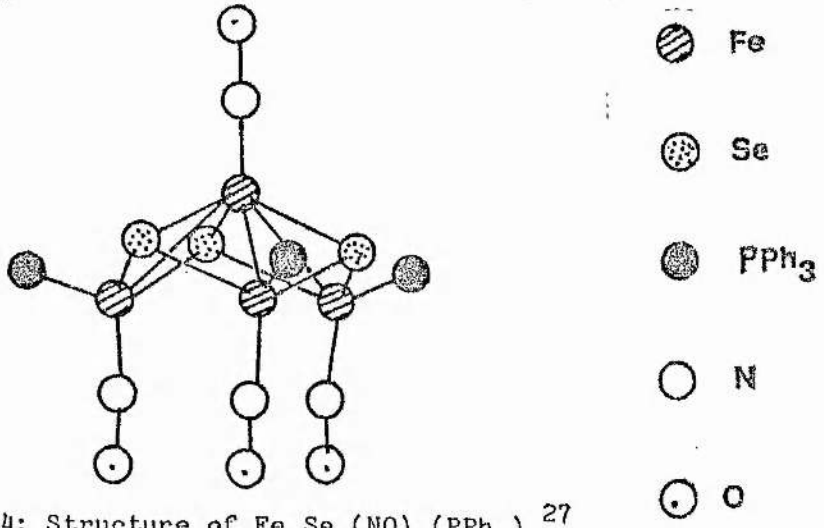


Fig. 1.4; Structure of $Fe_4Se_3(NO)_4(PPh_3)_3$[27].

In this complex, the nitrosyls of the basal iron atoms closest to the apical iron atom are replaced with triphenylphosphine. In an attempt to isolate a reduced salt of $Fe_4Se_3(NO)_4(PPh_3)_3$ by the action of various reducing agents, the dianion, $[Fe_4Se_3(NO)_7]^{-2}$ was isolated[27] and structurally characterised by X-ray crystallography. The $[Fe_4Se_3(NO)_7]^{-2}$ complex is structurally similar to that of $[Fe_4S_3(NO)_7]^-$. As would be expected, the major structural variation between the sulphur and selenium analogues is an increase in bond lengths; this is primarily due to the increase in the size of the

chalcogen atoms[27]. In addition to this cluster expansion the selenium cluster is distorted from the C_{3v} symmetry of $[Fe_4S_3(NO)_7]^-$ due to the presence of an extra electron. In the 'quantitative' molecular orbital examination[26] of $[Fe_4S_3(NO)_7]^-$, addition of electrons was found to weaken the cluster bonding resulting in a decrease in the Fe-Fe overlap population of 27%. It is calculated that addition of electrons to both $[Fe_4S_3(NO)_7]^-$ and $Fe_4S_4(NO)_4$ results in the occupancy of degenerate LUMO's of E and T_1 symmetry respectively resulting in Jahn-Teller sensitive ions. The $Fe_4Se_3(NO)_4(PPh_3)_3$ complex is structurally similar with that of both $[Fe_4S_3(NO)_7]^-$ and $[Fe_4Se_3(NO)_7]^{-2}$. The bond lengths in $[Fe_4Se_3(NO)_4(PPh_3)_3]$ are similar to those observed for $[Fe_4Se_3(NO)_7]^{-2}$ and the complex is, distorted from the C_{3v} symmetry of the monoanion $[Fe_4S_3(NO)_7]^-$.

In addition to the structural similarities demonstrated by chalcogen derivatives of iron-nitrosyl complexes, $[Fe_4S_3(NO)_7]^-$ possesses similarities with both $Fe_4S_4(NO)_4$ and $Fe_2(SEt)_2(NO)_4$. The apical iron of $[Fe_4S_3(NO)_7]^-$ resembles that of iron in $Fe_4S_4(NO)_4$ both in bond lengths and in bond angles (table 1.1),

Table 1.1: Interatomic bond distances and angles for the apical iron in $[Fe_4S_3(NO)_7]^-$ and for $Fe_4S_4(NO)_4$.

		$ON\text{-}Fe_AS_3(Fe_B)_3$	$Fe_4S_4(NO)_4$
Bond Lengths/Å	Fe_AS	2.21	2.22
	Fe_AN	1.64	1.66
	N-O	1.17	1.16
Bond Angles/°	$ON\text{-}\underline{Fe}_A\text{-}S$	112	114
	$S\text{-}\underline{Fe}_A\text{-}S$	108	104

whilst the three basal iron atoms have bond lengths and bond angles similar to those in $Fe_2(SR)_2(NO)_4$ (table 1.2).

Table 1.2; Interatomic bond distances for the basal iron in $[Fe_4S_3(NO)_7]^-$ and for $Fe_2(SEt)_2(NO)_4$.

		$(ON)_2Fe_BS_2Fe$	$Fe_2(SEt)_2(NO)_4$
Bond Lengths/Å	Fe_BS	2.26	2.27
	Fe_BN	1.64	1.67
	N-O	1.18	1.17
Bond Angles/°	ON-$\underline{Fe_B}$-NO	114	117
	S-$\underline{Fe_B}$-S	104	106

Examination of the three $Fe_BS_2Fe_A$ faces shows them to demonstrate close analogy to the iron sulphur plane in $Fe_2(SEt)_2(NO)_4$. The $[Fe_4S_3(NO)_7]^-$ complex has been described[3] as the fusion of three molecules of $[Fe_2S_2(NO)_4]^{-2}$ minus an NO from one of the two iron atoms.

1.2 Iron-Sulphur proteins, bis(μ_2-methanethiolato)-bis(dinitrosyliron) and China.

The requirement of all life forms for small quantities of certain metal ions termed 'trace elements' has been known for many years[38]. The number of elements in this list of essentials to life, as well as the list of their biological functions has steadily increased. The recent development of powerful physical and chemical structure probes

has facilitated the determination of the structure of the biological sites of some of these elements. X-ray analysis has been applied to determine both the coordination of metal ions in biological sites in isolated bioinorganic complexes and the sophisticated ways in which nature can control relatively flexible stereochemistry.

The major techniques applied to examine the properties of isolated bioinorganic compounds are EXAFS, Mössbauer, n.m.r., e.p.r. and u.v./visible spectroscopies combined in certain cases with isomorphic metal exchange[38].

Amongst the group of metals in bioinorganic compounds which have been extensively studied are zinc in carbonic anhydrase[39], cobalt in vitamin B_{12}[40], and iron in both haemoglobin[41] and iron-sulphur proteins[42]. This short list demonstrates some of the essential biological complexes in which these metals are found and how dependent all life forms are on these few elements and their complexes. Their biochemical importance demands their thorough investigation so that the mechanism of their activity may be determined. The study of these compounds is somewhat hampered by their often low concentrations in living matter, requiring painstaking extractions to obtain tiny quantities of material. Even when the bioinorganic complexes have been isolated their study can still be hindered by the large organic complex surrounding in some cases a single metal atom. The application of EXAFS is particularly useful for the observation of the metal centre in such complexes[43]. Nitrogenase is one of the enzymes involved in the fixation of nitrogen. In the enzyme there are six iron and two molybdenum atoms in a complex with an overall molecular

weight of about 220,000[44]. These metal ions, although just present as a trace in these complexes, are indispensible, their extraction resulting in enzyme deactivation.

The biological interest in bioinorganic complexes has led to much fruitful synthetic and mechanistic work in inorganic chemistry[45]. Prominent in the field of bioinorganic chemistry is the study of Fe-S proteins and, with the possible exception of heme proteins, no other class of metalloproteins has been as thoroughly investigated in the last decade.

Iron-sulphur proteins were discovered in the mid-1950's and are now known to be the most widely dispersed metalloproteins in nature[38]. The rôles which these complexes play are diverse. They are mainly involved in cellular oxidation processes, including photosynthesis and nitrogen fixation. These metalloproteins contain either one[46], two[47,48] (2Fe-2S), three[49] (3Fe-3S) or four[50] (4Fe-4S) iron atoms bound to protein chains by the thiol group of cysteine (fig. 1.5).

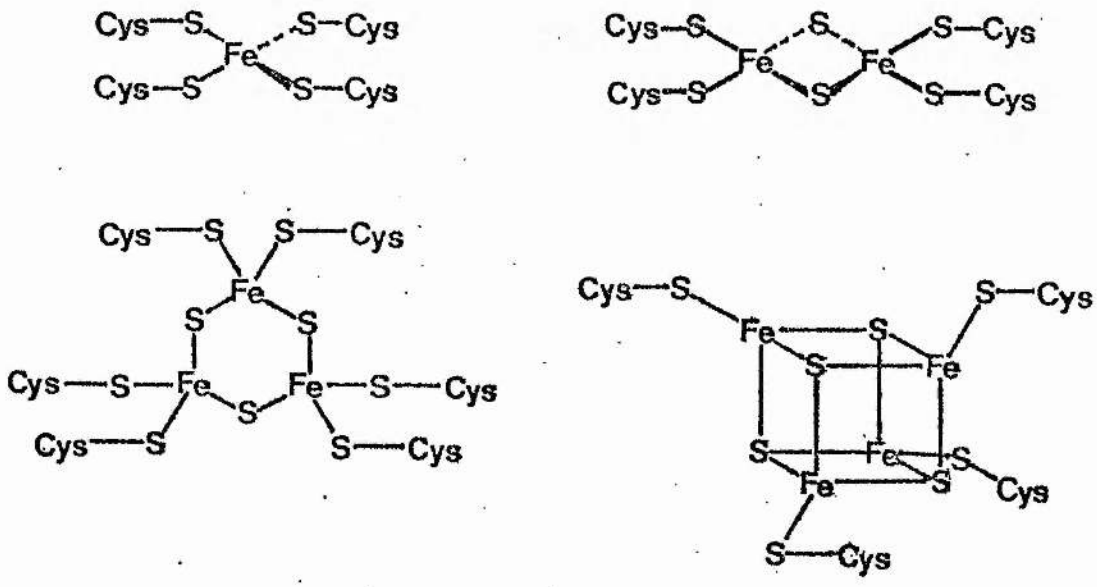


Fig. 1.5; Structures of 1-Fe, 2Fe-2S, 3Fe-3S, and 4Fe-4S iron-sulphur clusters[38].

In the multi-iron atom clusters 'acid labile' sulphur atoms bridge the constituent iron atoms. The iron atoms contained in these complexes are essentially tetrahedrally coordinated to four sulphur atoms[38]. Examination of the chemistry of these complexes has been greatly assisted by the discovery by Holm and coworkers of methods for the synthetic preparation of alkyl and arylthiolate analogues of the mono[51], di[52] and tetra[53] iron compounds. The model compounds give good structural and electronic representations of the isoelectronic protein sites[38].

The 2Fe-2S complexes act as one electron transfer agents. Mössbauer examination[54,55] of the oxidised form of the complex reveals a single oxidation state for the constituent iron atoms. This complex contains solely high spin Fe^{+3} and is diamagnetic at low temperatures, this is due to the unpaired electrons of each of the iron atoms possessing opposite spin to the other giving the appearance of spin pairing, the iron atoms being indirectly coupled through the bridging sulphur ligands. On a one electron reduction the complex becomes paramagnetic. Mössbauer examination of the complex yields two equivalent peaks, this is due to the localisation of the extra electron on one of the iron atoms, resulting in a complex containing Fe^{+2} and Fe^{+3}. This is unlike the one electron/reduction process in the ferredoxin 4Fe-4S complex[56] where the charge is delocalised over the cluster, as is expected for cluster compounds. Mössbauer examination of both the reduced and oxidised forms of the cluster reveals a single peak in each case. The oxidised form of ferredoxin contains $4(Fe^{+2.5})$ and the reduced form $4(Fe^{+2.25})$. This demonstrates

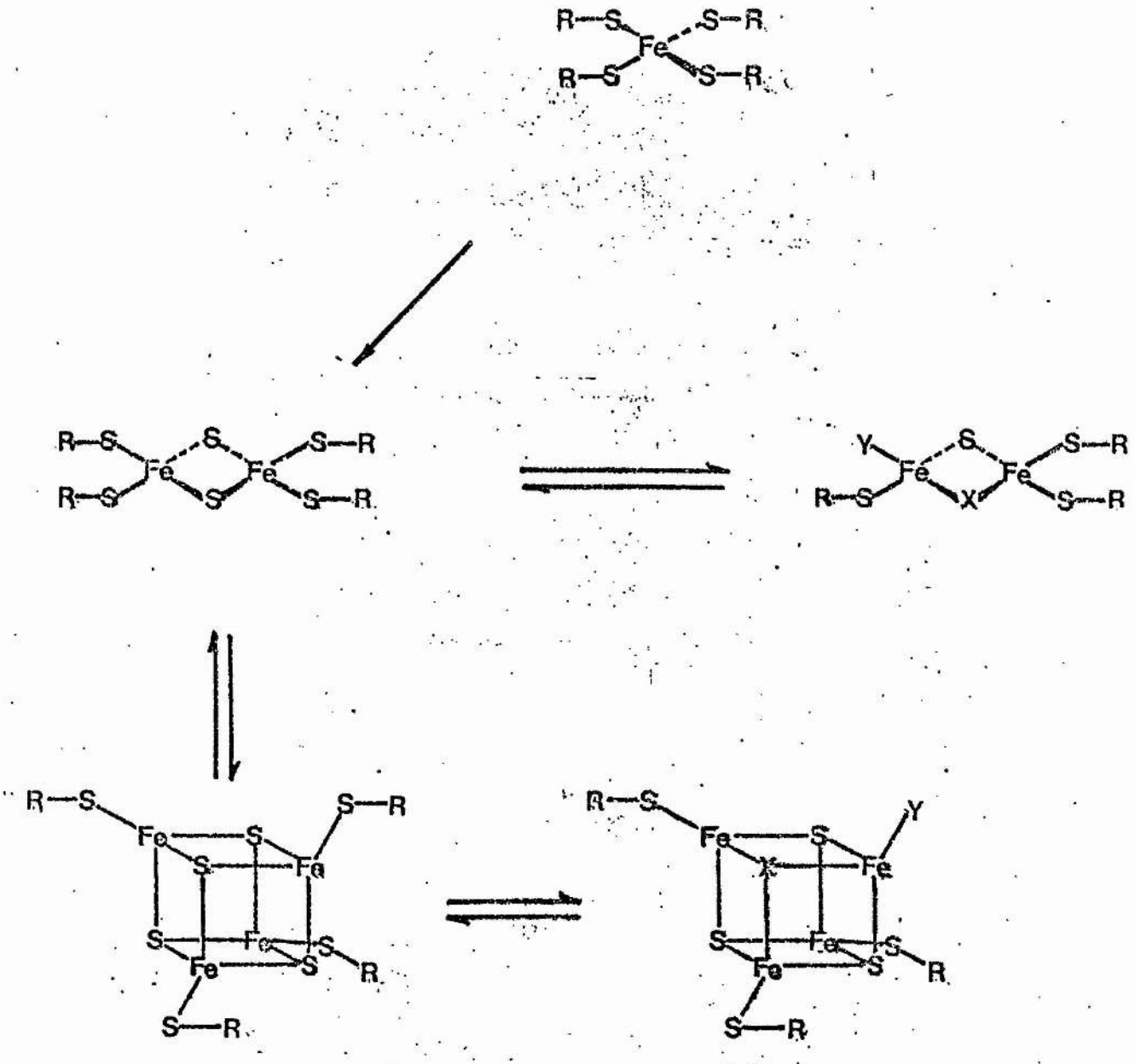


Fig. 1.6; Ligand exchange reactions for iron-sulphur complexes[58,59]

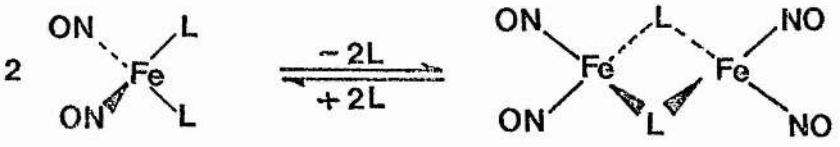
the caution which must be taken in the assignment of oxidation states and why in 1.1 above the apical iron atom in Roussins black salt is ascribed a 'formal' oxidation state of +1.

The formation of these synthetic models of iron-sulphur proteins has been described that of 'spontaneous self-assembly'[57] where the final products of the reactions could not have been predicted from the reactants. Holm and coworkers have demonstrated that these clusters are labile to reaction, both terminal-ligand[58] and core-atom[59] exchange can occur and the clusters are labile to interconversion (fig. 1.6)[38]. Ligand exchange is not confined solely to chalcogens; it has been found that ligands such as halides can be substituted in their place[60].

The isostructural analogue, $Fe_2(SMe)_2(NO)_4$ of the 2Fe-2S complexes has recently been implicated in carcinogenesis. As part of a large scale survey of various maladies of the population of China a study of the incidence of different forms of cancer was investigated[61]. Of particular note was a remarkably high incidence of cancer of the oesophagus in the Linxian region with one in four of the adult population affected. In an attempt to reduce this high incidence a study of both environmental and dietary factors was instigated. Three factors were discovered which could be responsible. The domestic water supply had both high concentrations of nitrate and nitrite, the soil had low concentrations of molybdenum and the peasants consumed 'pickled' cabbage. This 'pickled' cabbage is prepared by soaking cabbage under water in large earthen pots for several weeks in which time it partially rots and becomes covered in a

mould. From extracts of this cabbage it was possible to identify, by comparative GC/MS, the μ_2-alkylthiolate $Fe_2(SMe)_2(NO)_4$[62]. Whilst examination of extracts of either fresh cabbage or cabbage soaked in distilled water failed to yield this compound. These observations implicate the local water supply in the generation of these species. Extracts of the pickled cabbage were shown to contain at least one mutagenic compound[63,64], and studies on $Fe_2(SMe)_2(NO)_4$ itself indicated that it may act as a tumour promoter[65]. It has been suggested that the source of the iron in the $Fe_2(SMe)_2(NO)_4$ is the iron-sulphur proteins in the cabbage[61].

McDonald and coworkers[66] generated a series of paramagnetic mono-nitrosyl complexes with general stoichiometry $[Fe(NO)_2L_2]^-$ in solution from the reaction of iron(II) salts with nitric oxide in the presence of various anionic ligands(L). It has been suggested[66-71] that these species exist in equilibrium with Roussin ester-like diamagnetic dimers:



The majority of the paramagnetic species thus generated have g-values of *ca.* 2.03[66-71]. Several groups of Biochemists[72-75] have observed similar g-centres in cell cultures treated with nitrosylating agents and have assigned the paramagnetic species to $[Fe(NO)_2]^+$ coordinated to thiol containing proteins.

It is not inconceivable that the action of various nitrosylating agents on naturally occurring iron-sulphur clusters yields nitrosylated iron species which exist in a mononuclear $\rightleftharpoons$ dinuclear (paramagnetic $\rightleftharpoons$ diamagnetic) equilibrium.

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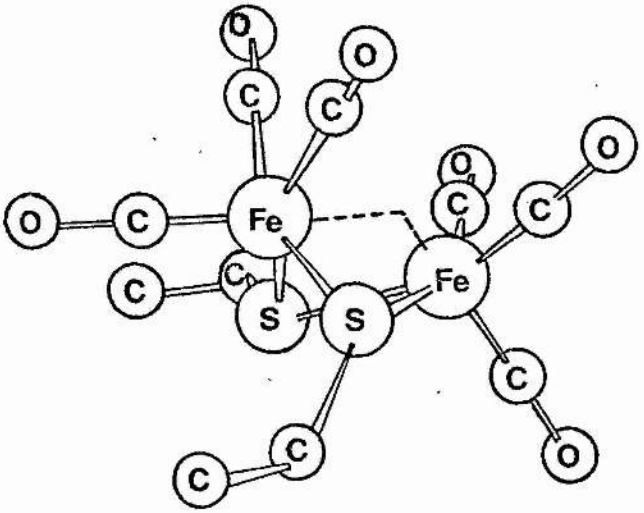


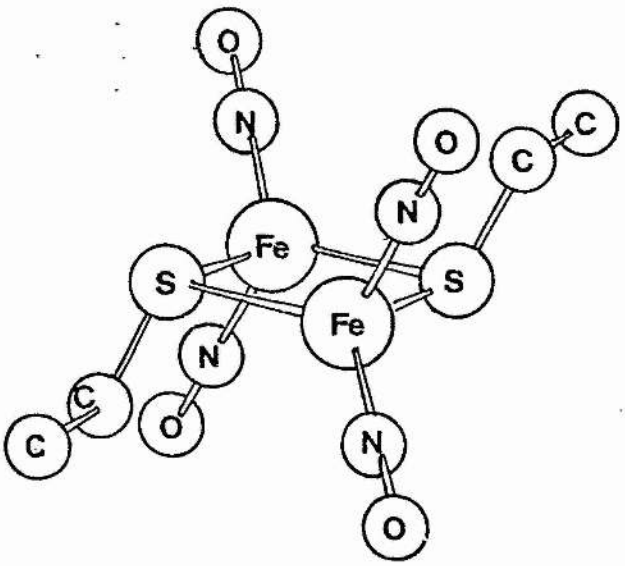


Fig. 2.1; Structures of $Fe_2(SEt)_2(CO)_6$[8] and $Fe_2(SEt)_2(NO)_4$[12].

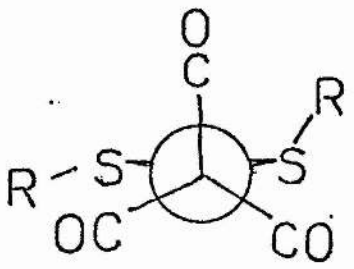
CHAPTER TWO

TERMINAL AND BRIDGING LIGAND EXCHANGE REACTIONS IN IRON-SULPHUR CARBONYLS.

2.1 Introduction.

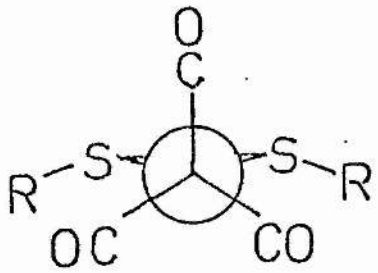
Reactions of various iron carbonyls with sulphides, thiols and disulphides to yield iron-sulphur carbonyls have been the centre of much research[1-7], which has concentrated primarily on structural elucidation in the solid state[7-11]. The products of these reactions consist in general of terminal carbonyl ligands bonded to an iron-sulphur core, but a marked diversity is found in the chemical behaviour of these compounds. Large structural reorganisations can occur, the products of which are unpredictable and can bear no resemblance to the structure of the precursor, and x-ray crystallography must be used for definitive characterisation. Chemical reactions, such as ligand exchange have also been reported where the overall structure remains basically unchanged.

The S-alkylated complex $Fe_2(SR)_2(CO)_6$[8] is closely analogous to the formally isoelectronic $Fe_2(SR)_2(NO)_4$[12], the structures having been determined for the ethyl ester of both (fig. 2.1). Comparison of the structures shows a marked difference in the Fe_2S_2 ring; this is planar with tetrahedral geometry about the iron atoms in the case of the nitrosyl, whilst in the carbonyl complexes the Fe_2S_2 ring is puckered. The existence of a bent iron-iron bond has been discussed

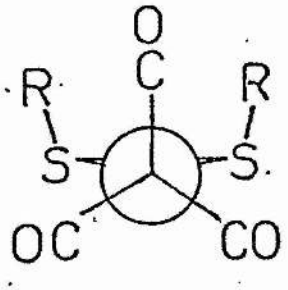


2.2.1. anti

(Fischer projection along Fe-Fe bond)

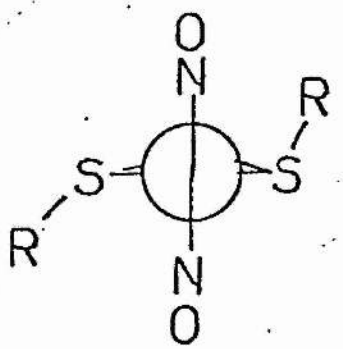


2.2.2. syn

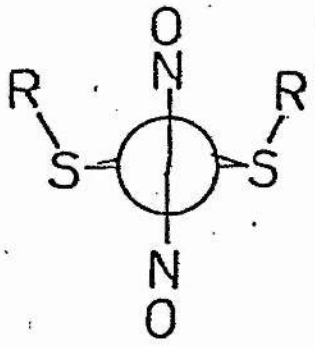


2.2.3. syn

Fig. 2.2; conformations of $Fe_2(SR)_2(CO)_6$.



C_{2h}



C_{2v}

Fig. 2.3; The two conformations of $Fe_2(SR)_2(NO)_4$[14,16].

in the literature[8] as being due to the carbonyl ligands maintaining octahedral coordination. Both compounds illustrate structural isomerism[13,14]. The carbonyl can exist in one of three configurations (fig. 2.2). All three have been observed for the "acid"[15] $Fe_2(SH)_2(CO)_6$, but, for the alkyl esters, only two have been observed and isolated[13]. These are the anti configuration (2.2.1) and presumably the syn configuration (2.2.2), the syn configuration (2.2.3) being less likely on stereochemical grounds. The nitrosyls have been observed to exist in one of two configurations in solution (fig. 2.3)[14,16]; and this is discussed in further detail in chapter 3.

Further analogies between iron carbonyls and nitrosyls are provided by the anions $[Fe_2S_2(CO)_6]^{-2}$ and $[Fe_2S_2(NO)_4]^{-2}$ [17] and by the uncharged cubane-type clusters $Fe_4S_4(CO)_{12}$[18] and $Fe_4S_4(NO)_4$[19]. The structures of the anions have been assumed to be similar to those of their alkyl derivatives, and this has been found to be true for the nitrosyl. Likewise the cubane analogues have been shown to possess certain structural similarities.

The conversion of iron carbonyls to nitrosyls has been known for over fifty years[20]; however, until recently little interest has been shown in the conversion of iron-sulphur carbonyls to their nitrosyl analogues. The purpose of the study reported in this chapter was to attempt this conversion and to exploit this as a method in preparing a series of derivatives $Fe_2(SR)_2(NO)_4$ from the analogous readily accesible and relatively stable carbonyl complexes. An exchange reaction between $Fe_2(SR)_2(NO)_4$ with R'_2S_2 is also examined as a method

for synthesising carbonyl esters from preformed iron-sulphur carbonyls and the results of this study are discussed.

2.2 Experimental.

2.2.1 Instruments and Materials.

Literature methods were employed for the preparation of $Fe_2(SR)_2(CO)_6$[13], $Fe_3S_2(CO)_9$[21], $Fe_2S_2(CO)_6$[21], $[Fe_2S_2(CO)_6]^{-2}$ [17], and $[PPN](NO_2)$[22] [PPN=$(Ph_3P)_2N^+$].

All solvents used were dried by conventional methods. Solutions for e.p.r. examination were prepared in an atmosphere of nitrogen.

^1H n.m.r. and ^{13}C n.m.r. were performed on a Bruker WP-80 and a Varian CFT-20. Infra-red spectra were obtained either as nujol mulls or solutions in chloroform on a Perkin-Elmer 1330 spectrometer. Mass spectra were obtained on an AEI MS 902. E.p.r. spectra were recorded on a Bruker ER 200D spectrometer.

2.2.2 Bridging Ligand exchange reactions of $Fe_2(SR)_2(CO)_6$.

The experiments recorded in this section were performed in conjunction with Seymour.

(a) Reaction of $Fe_2(SMe)_2(CO)_6$ with Et_2S_2. $Fe_2(SMe)_2(CO)_6$ (2.0g; 5.3 mmol) was refluxed with ethyl sulphide (3 ml; 25 mmol) in benzene (50

ml) under nitrogen for one hour. This mixture was reduced to solid and pumped on the vacuum system for eight hours to remove any residual alkyl sulphides. The residual solid was dissolved in 40-60 petroleum ether and cleaned up on a 15 cm x 1.5 cm alumina chromatography column, eluting with petrol. The eluent was reduced to solid and examined by mass spectroscopy to reveal the mixture to be composed largely of $Fe_2(SMe)_2(CO)_6$ with some $Fe_2(SEt)(SMe)(CO)_6$, but no $Fe_2(SEt)_2(CO)_6$. The mixture was redissolved in benzene (50 ml) and refluxed under nitrogen with ethyl sulphide (3 ml; 25 mmol) for a further six hours. This mixture was worked up as described above and examined by mass spectrometry. This revealed $Fe_2(SEt)_2(CO)_6$ as the major component, with trace quantities of $Fe_2(SMe)(SEt)(CO)_6$ $Fe_2(SMe)_2(CO)_6$.

The above reaction was repeated with a continuous reflux for 72 hours, samples were taken after 5, 10, 20, and 30 minutes, 1, 2, 4, 6, 12, 24, 36, 48, 60, and 72 hours and examined by GCMS and comparative GLC (10% S.E. 30; 80°C) with authentic samples of Me_2S_2, MeSSEt and Et_2S_2 and GC/MS. After one hour the presence of MeSSEt was detected. With continued reflux the relative concentration of MeSSEt to Et_2S_2 was observed to increase. It was only in the later stages of the exchange reaction (t>8 hours) was the presence of Me_2S_2 detected.

This exchange reaction was repeated with Bz_2S_2 ($Bz=CH_2Ph$) and $Fe_2(SEt)_2(CO)_6$. Attempts were made also to examine an exchange reaction between $Fe_2(SEt)_2(CO)_6$ and BzSH and also $Fe_2(SMe)_2(CO)_6$ and BzSH, in both cases these were unsuccessful.

Analysis. Typical mass spec. $Fe_2(SMe)_2(CO)_6$: M/z 374 (molecular ion);

346; 318; 290; 262; 234; 206 (sequential loss of 6 CO); 191, 176 (sequential loss of 2 Me). ^{1}H n.m.r. 2.17(s), 2.20(s), 1.64(s) p.p.m. (see appendix 2 for further examples). T.l.c., two orange spots (one for each conformer in petrol on silica gel (Rf=0.9 and 0.7). I.r. strong absorptions ca. 2000 cm^{-1}.

(b) Reaction of $Fe_3(CO)_{12}$ with $(MeOCOCH_2S)_2$. $(MeOCOCH_2S_2)_2$ was refluxed with $Fe_3(CO)_{12}$ to yield $Fe_2(SCH_2CO_2Me)_2(CO)_6$ as literature for the preparation of $Fe_2(SR)_2(CO)_6$[13]. Examination of the resultant mixture by both t.l.c. and mass spectroscopy revealed the presence of both $Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$. Isolation of these two components and reflux with either Me_2S_2 or $(MeOCOCH_2S)_2$ failed, even after prolonged reflux to yield $Fe_2(SR)_2(CO)_6$. Examination of the reaction of $Fe_3(CO)_{12}$ with Me_2S_2 with time by both t.l.c. and mass spectroscopy failed to reveal the presence of any $Fe_3S_2(CO)_9$ or $Fe_2S_2(CO)_6$.

Analysis. $Fe_2S_2(CO)_6$. Mass spec., M/z 344 (molecular ion); 316; 288; 260; 232; 204; 176 (sequential loss of 6 CO). T.l.c., Yellow spot, Rf=0.7 in petrol on silica gel. I.r., strong absorptions ca. 2000 cm^{-1}.

$Fe_3S_2(CO)_9$. Mass spec., M/z 484 (molecular ion); 456; 428; 400; 372; 344; 316; 288; 260; 232 (sequential loss of 6 CO). T.l.c., purple spot, Rf=0.6 in petrol on silica gel. I.r., strong absorptions ca. 2000 cm^{-1}.

2.2.3 Carbonyl-Nitrosyl ligand exchange.

A series of different carbonyl-nitrosyl exchange reactions were examined as outlined below. The results of these examinations are listed in table 2.1.

(a) Reaction with alkaline/acidic nitrite. In a typical reaction, the carbonyl complex (24 mmol) and sodium nitrite (6.0g) were added to a solution of sodium hydroxide (10.0g) in a mixture of water (50 ml) and ethanol (25 ml). the mixture was refluxed under nitrogen for two hours resulting in a green solution. This mixture was allowed to cool to ca. 30°C and then acidified with a 1:1 (v/v) glacial acetic acid/water mixture. The resulting mixture was evaporated to dryness and the resultant solid extracted firstly with CH_2Cl_2 (6 x 50 ml), and secondly with water (2 x 100 ml). the methylene chloride extract was washed with water (2 x 50 ml), dried over Na_2SO_4, and evaporated to dryness: recrystallisation from 1:1 CH_2Cl_2/MeOH yielded $Fe_2(SR)_2(NO)_4$. The aqueous extract was extracted with ether (4 x 50 ml), and the ether layer was dried over Na_2SO_4, and evaporated to dryness to yield $[Fe_4S_3(NO)_7]Na$: to the residual aqueous solution was added aqueous $Ph_4As^+Cl^-$; the resulting precipitate was filtered, and dissolved in CH_2Cl_2 washed with water (2 x 50 ml), and dried over Na_2SO_4. This mixture was reduced to solid and recrsytallised from CH_2Cl_2/petrol mixture to yield $(AsPh_4)_2[Fe_2S_2(NO)_4]$

Analysis;$Fe_2(SR)_2(NO)_4$: I.r. ν(N-O)/cm^{-1} 1815w, 1780s, 1750s. Mass spectrum M/z 326 (molecular ion); 296, 266, 236, 206 (sequential loss of 4 NO); 191, 176 (sequential loss of 2 Me). T.l.c. single spot in

chloroform on silica gel (Rf=0.7). Anal. $Fe_2(SMe)_2(NO)_4$: Found, C, 7.56%; H, 1.84%; N, 15.48%. Calc. for $C_2H_6N_4O_4S_2Fe_2$: C, 7.37%; H, 1.86%; N, 17.19%.

$[Fe_4S_3(NO)_7]^-$: I.r. ν(N-O)/cm^{-1} 1790m, 1720s, and 1690m. T.l.c. single spot in methanol on silica gel (Rf=1.0). U.v. λ/nm (mol^{-1} cm^{-1}) 560 (2400), 350 (15400), 260 (26700). Anal. $[Fe_4S_3(NO)_7](Ph_4As)$: Found, C, 31.54%; H, 2.19%; N, 10.59%. Calc. for $C_{24}H_{20}N_7O_7AsFe_4S_3$: C, 31.57%; H, 2.21%; N, 10.74%.

$[Fe_2S_2(NO)_4]^{-2}$: I.r. ν(N-O)/cm^{-1} 1810w, 1778s, and 1754m. T.l.c. initial red spot, turns to brown spot on silica gel (due to conversion to $[Fe_4S_3(NO)_7]^-$). Anal. $[Fe_2S_2(NO)_4](AsPh_4)_2$: Found, C, 54.41%; H, 3.84%, N 5.20%. Calc. for $C_{48}H_{20}N_4O_4As_2Fe_2S_2$: C, 54.21%; H, 3.80%, N 5.27%.

(b) Reaction with nitric oxide. Typically, the carbonyl complex (10 mmol) was dissolved in $CHCl_3$ (50 ml), and the solution purged with nitrogen. Nitric oxide was bubbled through the solution for 1 hour, and the solution was reduced to dryness. The work-up then follows that described above in (a). Examination of this reaction at different temperatures revealed that optimised yields were obtained by refluxing the mixture whilst bubbling nitric oxide.

(c) Reaction with nitric oxide in the presence of alkali/acid. The procedure employed was essentially that described in (a) above, except that the nitrogen stream was replaced by nitric oxide and the sodium nitrite was omitted from the reaction medium.

(d) Reaction of $PPN[NO_2]$ and $NaNO_2$ with $Fe_2(SR)_2(CO)_6$.

(i) Reaction with $NaNO_2$. In a typical reaction, $Fe_2(SR)_2(CO)_6$ (1.3 mmol) and $NaNO_2$ (0.50g, 7.1 mmol) were refluxed in 30 ml of dry redistilled DMF for 30 minutes under nitrogen, and then cooled to 100°C. 500 ml of dry redistilled toluene was added, causing conversion of green $[Fe(NO)_2(SR)_2]^-$ to red $Fe_2(SR)_2(NO)_4$. This mixture was filtered and the filtrate evaporated to dryness: the residue was dissolved in CH_2Cl_2 (40 ml) and the solution washed with water (10 x 300 ml). The organic fraction was dried over Na_2SO_4, filtered, and reduced to small volume. The dark red product was precipitated by addition of an equal volume of ice-cold methanol. The average yield for the reaction was 25%.

(ii) Reaction with $PPN(NO_2)$. To THF solutions containing $Fe_2(SR)_2(NO)_4$ under nitrogen, was added equimolar quantities of $PPN(NO_2)$. Over a half an hour peroid this mixture darkened in colour. Extracts of this solution were examined by e.p.r. spectroscopy to reveal the presence of paramagnetic mono-iron fragments. However, all attempts to isolate these resulted in the sole isolation of $Fe_2(SR)_2(NO)_4$.

2.3 Results and Discussion.

2.3.1 Bridging ligand exchange in $Fe_2(SR)_2(CO)_6$.

Alkyl disulphides react with $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ to yield $Fe_2(SR)_2(CO)_6$ in a synthetically useful reaction[23]. An attractive possibility for the formation of $Fe_2(SR')_2(CO)_6$ in cases where the disulphide R'_2S_2 is of low volatility whilst that of R_2S_2 is high is the exchange reaction:

$$Fe_2(SMe)_2(CO)_6 + RSSR \longrightarrow Me_2S_2 + Fe_2(SR)_2(CO)_6$$

In this chapter the results of an examination of the feasibility of this reaction are reported.

Reflux of a mixture of $Fe_2(SMe)_2(CO)_6$ with an excess of Et_2S_2 resulted in the isolation of $Fe_2(SEt)_2(CO)_6$. Examination of the products of this reaction by mass spectrometry revealed that the reaction proceeded by an initial formation of the mixed ester $Fe_2(SMe)(SEt)(CO)_6$ followed subsequently by formation of $Fe_2(SEt)_2(CO)_6$.

$$Fe_2(SR)_2(CO)_6 \xrightarrow{Et_2S_2} Fe_2(SMe)(SEt)(CO)_6$$

$$Fe(SMe)(SEt)(CO)_6 \xrightarrow{Et_2S_2} Fe_2(SEt)_2(CO)_6$$

Concurrent with the formation of $Fe_2(SMe)(SEt)(CO)_6$ the generation of

the mixed disulphide MeSSEt was detected by GC/MS: only at a fairly late stage in the reaction was a significant quantity of Me_2S_2 detected.

There are several distinct mechanistic possibilities for the formation of the mixed ester $Fe_2(SMe)(SEt)(CO)_6$ in the exchange reaction. A possible route would be by ring fission of $Fe_2(SMe)_2(CO)_6$ and $Fe_2(SEt)_2(CO)_6$ followed by recombination. Reflux of an equimolar mixture of $Fe_2(SMe)_2(CO)_6$ and $Fe_2(SEt)_2(CO)_6$ in benzene resulted in the isolation of the mixed ester. However, this took considerably longer than that observed in the reaction of $Fe_2(SMe)_2(CO)_6$ with Et_2S_2. If the mixed ester were to be generated by a ring fission process it would require the initial formation of $Fe_2(SEt)_2(CO)_6$, which was observed to be generated after the formation of $Fe_2(SMe)(SEt)(CO)_6$; hence this process may be disregarded. Likewise exchange between Me_2S_2 and Et_2S_2 under the same reaction conditions occurred very slowly, and for effective exchange to occur the presence of a catalytic quantity of RS^-/HS^- is necessary[24]. Hence, it can be assumed that exchange must occur *via* a stepwise replacement of SR groups.

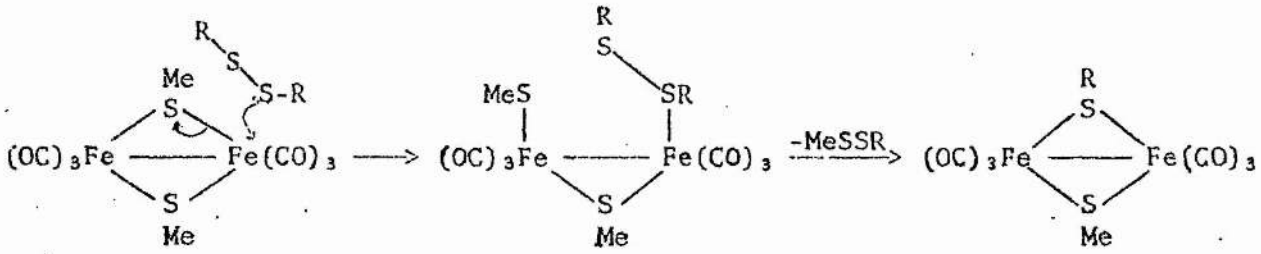
$$Fe_2(SR)_2(CO)_6 + R'_2S_2 \longrightarrow Fe(SR)(SR')(CO)_6 + RSSR'$$

$$Fe_2(SR)(SR')(CO)_6 + R'_2S_2 \longrightarrow Fe(SR')_2(CO)_6 + RSSR'$$

In addition to the examination of the exchange reaction between $Fe_2(SMe)_2(CO)_6$ and Et_2S_2, the reaction of $Fe_2(SEt)_2(CO)_6$ and Bz_2S_2 (Bz=$PhCH_2$) was examined, this resulted in the formation of $Fe_2(SBz)_2(CO)_6$ with the observation of a mixed ester intermediate $Fe_2(SEt)(SBz)(CO)_6$ and the detection of both BzSSEt and Et_2S_2. Repeating this study substituting BzSH for Bz_2S_2 failed, even after prolonged reflux, to yield either $Fe_2(SBz)_2(CO)_6$ or $Fe_2(SEt)(SBz)(CO)_6$. Since benzyl mercaptan was found not to exchange in the solvent system examined, despite the volatility of EtSH

$$Fe_2(SEt)_2(CO)_6 + BzSH \xrightarrow{X} EtSH + Fe_2(SEt)(SBz)(CO)_6$$

it can be concluded that the exchange reaction depends upon the sulphur's nucleophilicity (α-effect) which arises from the two adjacent sulphur atoms in the disulphide. A reaction scheme can be proposed:



The alkyl esters of both types $Fe_2(SR)_2(CO)_6$ and $Fe_2(SR)_2(NO)_4$, are insoluble in water, and one of the objects of this study was to develop synthetic routes to water soluble iron-sulphur carbonyls prior to the conversion to their analogous nitrosyl. By application of a

suitably functionalised disulphide in this ligand exchange process the resultant carbonyl should demonstrate good solubility characteristics. $(MeOCOCH_2S)_2$ was chosen for exchange as a convenient preliminary to employing $(HOCOCH_2S)_2$: use of the acid should result in a very water soluble complex. However, it was found that even after extended reflux of $Fe_2(SMe)_2(CO)_6$ with $(MeOCOCH_2S)_2$ in benzene no exchange products were detected. This reduction of reactivity may have been due to the carboxyl group reducing the supernucleophilicity of the disulphide. To determine whether $Fe_2(SCH_2COOMe)_2(CO)_6$ could be formed, the reaction of the disulphide with $Fe_3(CO)_{12}$ was examined. Reaction of $(MeOCOCH_2S)_2$ with $Fe_3(CO)_{12}$ yielded $Fe_2(SCH_2COOMe)_2(CO)_6$, but in addition $Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$ were also isolated. It was also found that refluxing a mixture of $Fe_3(CO)_{12}$ and elemental sulphur yielded a mixture of $Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$. However, since the reaction was performed in sulphur free benzene, it must be assumed that a sulphur extraction must have occurred. Reflux of either $(MeOCOCH_2S)_2$ or Me_2S_2 with $Fe_2S_2(CO)_6$, $Fe_3S_2(CO)_9$, or a mixture of both failed to yield any S-alkylated iron carbonyl products. It follows therefore that $Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$ are not intermediates in the formation of $Fe_2(SR)_2(CO)_6$. In the examination of their formation in the reaction of $(MeOCOCH_2S)_2$ with $Fe_3(CO)_{12}$ these complexes were detected very quickly, and subsequent reflux of the mixture resulted in a decrease in their concentration (due to thermal decomposition) and it can be assumed that the complexes are formed initially rather than by a secondary reaction from $Fe_2(SR)_2(CO)_6$.

Table 2.1: Nitrosylation Reactions

Reactant	Method[a]	Product	Yield/%
$Fe_2(CO)_9$	A	$Fe(CO)_2(NO)_2$	b
$Fe_3(CO)_{12}$	A	$Fe(CO)_2(NO)_2$	b
$Fe_2(SMe)_2(CO)_6$	A	$Fe_2(SMe)_2(NO)_4$	33
$Fe_2(SMe)_2(CO)_6$	B	$Fe_2(SMe)_2(NO)_4$	92
$Fe_2(SMe)_2(CO)_6$	C	$Fe_2(SMe)_2(NO)_4$	25
$Fe_2(SEt)_2(CO)_6$	A	$Fe_2(SEt)_2(NO)_4$	33
$Fe_2(SEt)_2(CO)_6$	B	$Fe_2(SEt)_2(NO)_4$	90
$Fe_2(SPr^i)_2(CO)_6$	B	$Fe_2(SPr^i)_2(NO)_4$	95
$Fe_2(SPr^i)_2(CO)_6$	C	$Fe_2(SPr^i)_2(NO)_4$	25
$Fe_2(SBz)_2(CO)_6$	B	$Fe_2(SBz)_2(NO)_4$	91
$Fe_2S_2(CO)_6$	A	$Fe_4S_3(NO)_7^-$	79
$Fe_2S_2(CO)_6$	B	No reaction	-
$Fe_2S_2(CO)_6^{-2}$	A	$Fe_4S_3(NO)_7^-$	82
		$Fe_2S_2(NO)_4^{-2}$	9
$Fe_2S_2(CO)_6^{-2}$	B	c	-
$Fe_3S_2(CO)_9$	A	$Fe_4S_3(NO)_7^-$	53
$Fe_3S_2(CO)_9$	D	$Fe_4S_3(NO)_7^-$	81
$Fe_3S_2(CO)_9$	B	No reaction	-

a. Method A: Reflux in aqueous alkaline/acidic nitrite. Method B: Application of nitric oxide. Method C: Reaction with nitrite in DMF. Method D. Reaction with nitric oxide in alkali/acid.

b. Volatile product; yield not measured.

c. Trace only of nitrosylated product, not identified.

In conclusion, a ligand exchange process between $Fe_2(SR)_2(CO)_6$ and R'_2S_2 exists, although it appears not to be general since exchange between $Fe_2(SMe)_2(CO)_6$ and $(MeOCOCH_2S)_2$ was not achieved: it did however prove possible to synthesise $Fe_2(SCH_2CO_2Me)_2(CO)_6$ from $Fe_3(CO)_{12}$ and $(MeOCOCH_2S)_2$.

2.3.2 Nitrosylation Reactions.

Stepwise replacement of carbonyl ligands by nitrosyls may be facilitated by treatment of $Fe(CO)_5$ with alkaline nitrite to yield the mono-nitrosyl complex $[Fe(CO)_3NO]^-$, (which is isolable as its mercury derivative[25] $Hg[Fe(CO)_3NO]_2$): acidification of this alkaline mixture in the presence of further nitrite yields $Fe(CO)_2(NO)_2$[25]. Further substitution is difficult, but possible, as photolysis of $Fe(CO)_2(NO)_2$ in the presence of nitric oxide yields $Fe(CO)(NO)_3$[26].

In the formation of $Fe(CO)_2(NO)_2$ from $Fe(CO)_5$, three carbonyl ligands are replaced by two nitrosyls. Several iron-sulphur carbonyls exist with three carbonyl ligands terminally bonded to iron, and thus this exchange reaction of three carbonyl ligands for two nitrosyl ligands is an attractive possibility for the formation of new iron-sulphur nitrosyls.

$$FeL_x(CO)_3 \longrightarrow FeL_x(NO)_2$$

In this section the results of the reaction between a selection of

iron carbonyls and alkaline/acidic nitrite and nitric oxide is reported.

Both $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ were treated with alkaline/acidic nitrite to test the generality of nitrosylation reaction. In both cases the sole iron-nitrosyl product isolated was $Fe(CO)_2(NO)_2$. No di-iron or tri-iron-nitrosyl carbonyl species were either isolated or detected in the reaction. The isolation of the mono-iron species $Fe(CO)_2(NO)_2$ is not particularly surprising since both $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ react with nitric oxide[20] under milder conditions to yield $Fe(CO)_2(NO)_2$.

Previous work in this laboratory[27,28] has shown that nitric oxide reacts with $Fe_2(SMe)_2(CO)_6$ at room or low temperatures to yield $Fe_2(SMe)_2(NO)_4$. However, in these studies the reaction was found to proceed slowly and low yields were obtained. Repeating this study and examining the reaction mixture with time by both t.l.c. and i.r. spectroscopy revealed no other species apart from $Fe_2(SMe)_2(CO)_6$ and $Fe_2(SMe)_2(NO)_4$. The absence of any detectable mixed carbonyl nitrosyl complexes, suggests that these complexes are more labile to exchange than the parent $Fe_2(SMe)_2(CO)_6$. Mixed carbonyl nitrosyl intermediates must exist, since for complete exchange to occur in one step, a fifth order reaction is required, the probability of which is rather low. It was found that by the simple expedient of refluxing the reaction mixture whilst bubbling nitric oxide, a relatively quick and complete conversion of the carbonyl to the analogous nitrosyl was achieved.

$$Fe_2(SR)_2(CO)_6 \xrightarrow{NO} Fe_2(SR)_2(NO)_4$$

The exchange reaction was repeated with both $Fe_2(SEt)_2(NO)_4$ and $Fe_2(SBz)_2(NO)_4$, and in each case high yields of the analogous nitrosyl was obtained.

To determine the nature of the intermediates of the nitrosylation reaction, an equimolar mixture of $Fe_2(SMe)_2(CO)_6$ and $Fe_2(SEt)_2(CO)_6$ was nitrosylated with nitric oxide. Examination of the mixture with time using mass spectrometry showed that the carbonyl-nitrosyl exchange proceeded at essentially the same rate for the two compounds and that no $Fe_2(SMe)(SEt)(CO)_6$ or $Fe_2(SMe)(SEt)(NO)_4$ was formed. The absence of the mixed ester implies that the iron-sulphur ring remains intact both by the action of refluxing in chloroform and during carbonyl-nitrosyl exchange. No detailed mechanistic studies were performed for the exchange reaction, but it should be noted that $Fe_2(SR)_2(CO)_6$ is stable to reflux in chloroform, suggesting that the reaction:

$$Fe_2(SR)_2(CO)_6 \longrightarrow [Fe_2(SR)_2(CO)_{6-x}] + xCO$$

is unlikely since carbon monoxide would be lost from the system, which would lead to the eventual decomposition of the carbonyl complex. It can therefore be inferred that the initial carbonyl-nitrosyl exchange occurs by a bimolecular process.

Dahl[7] has used a high pressure gaseous exchange reaction in the preparation of $Fe_4S_4(CO)_{12}$ from $Fe_4S_4(NO)_4$. Attempts to convert $Fe_2(SR)_2(NO)_4$ to $Fe_2(SR)_2(CO)_6$ by the bubbling of carbon monoxide through a refluxing solution of the nitrosyl in chloroform proved unsuccessful. After three hours bubbling no carbonyl complex could be detected by i.r. spectroscopy and the resultant work up of the solution yielded $Fe_2(SR)_2(NO)_4$ in an almost quantitative recovery.

In addition to the examination of the carbonyl-nitrosyl conversion of $Fe_2(SR)_2(CO)_6$ by means of nitric oxide, alkaline/acidic nitrite was examined as a method for preparing the nitrosyl analogues from the carbonyls. Reaction of $Fe_2(SMe)_2(NO)_4$ with aqueous alkaline nitrite yielded a green solution; addition of acid to this in the presence of nitrite resulted in the generation of a red solution: the carbonyl complex was completely converted to isolable $Fe_2(SR)_2(NO)_4$. The yields obtained were comparable with those obtained by use of nitric oxide at room temperature, but low in comparison with that obtained using nitric oxide at elevated temperatures. If the same exchange process occurs with $Fe_2(SMe)_2(CO)_6$ as that proposed for the conversion of $Fe(CO)_2(NO)_2$, then an intermediate such as $[Fe(SR)(CO)(NO)]^-$ might be expected after treatment with alkaline nitrite. Attempts to isolate such a complex proved unsuccessful. Although $[Fe(CO)_3(NO)]^-$ can be isolated as a mercury(II) derivative ($[Fe(CO)_3(NO)]_2Hg$), a similar isolation procedure could not be applied to the putative ion $[Fe(SR)CO(NO)]^-$ since mercury salts readily oxidise iron-sulphur nitrosyls[27].

A recent publication has shown that the action of $PPN[NO_2]$ on $Fe(CO)_5$ in THF yields $[Fe(CO)_3(NO)](PPN)$ in high yields. This reaction was repeated substituting $Fe_2(SR)_2(CO)_6$ for $Fe(CO)_5$. Examination of the green reaction mixture after addition of a 2:1 molar ratio of $[PPN](NO_2)$ to $Fe(SR)_2(CO)_6$ resulted in the observation of a paramagnetic mono-iron complex (g=2.022; A=1.6G). This implies that the nitrosylation reaction involving nitrite proceeds via a ring fission process. Insufficient hyperfine coupling was obtained fully to assign the paramagnetic complex, but hyperfine coupling to two nitrosyls was resolved. Attempts to isolate this mono-iron species proved unsuccessful, but $Fe_2(SR)_2(NO)_4$ was readily isolated. If the aqueous reaction is identical to that observed with $[PPN](NO_2)$ then the initial alkaline stage results in ring fission followed by substitution of two rather than one nitrosyl ligand. In chapters 4,5 and 6, the results of the examination of various $[Fe(NO)_2L_2]^-$ (L=chalcogen,halogen,pseudohalogen) complexes are discussed; in general it is found that these complexes were green, whilst the $Fe_2(SR)_2(NO)_4$ dimers were red. The $[Fe(NO)_2L_2]^-$ complexes were found to exist in a pH dependent equilibrium with $Fe_2L_2(NO)_4$ the dinuclear complex being favoured in acid. This implies that the addition of acid in the conversion reaction was required solely to adjust this equilibrium to yield the relatively stable dimer.

In conjunction with the study of the carbonyl-nitrosyl exchange reaction for $Fe_2(SR)_2(CO)_6$, the iron-sulphur carbonyls $Fe_2S_2(CO)_6$, $[Fe_2S_2(CO)_6]^{-2}$ and $Fe_3S_2(CO)_9$ were also examined. $[Fe_2S_2(CO)_6]^{-2}$ is isoelectronic with Roussin's Red anion, $[Fe_2S_2(NO)_4]^{-2}$, whilst

$Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$ have no previously identified structural nitrosyl analogues. Attempts to nitrosylate these three complexes with nitric oxide effected negligible reaction. Repeating these reactions by application of the aqueous nitrite method yielded in all three cases $[Fe_4S_3(NO)_7]^-$, although some $[Fe_2S_2(NO)_4]^{-2}$ was isolated in the case of the dianion $[Fe_2S_2(CO)_6]^{-2}$. Repeating these reactions with $[PPN](NO_2)$ resulted in the generation of paramagnetic mono-iron species, similar to those generated from $Fe_2SR_2(CO)_6$. If the mechanism of carbonyl-nitrosyl exchange in these three compounds proceeds via a common mono-iron intermediate then the isolation of a common product is not particularly surprising. Since the mono-iron $[Fe(NO)_2L_2]^-$ fragments exist in an acid base equilibrium with their dimers:

$$2[Fe(NO)_2L_2]^- \rightleftharpoons Fe_2L_2(NO)_4 + 2L^-$$

the expected product from these reactions is therefore $[Fe_2S_2(NO)_4]^{-2}$. However, $[Fe_4S_3(NO)_7]^-$ and $[Fe_2S_2(NO)_4]^{-2}$ exist in an acid/base equilibrium[29,30], $[Fe_4S_3(NO)_7]^-$ being favoured in acid. Since the final step of these nitrosylation reactions involves application of acid, the isolation of $[Fe_4S_3(NO)_7]^-$ as the major product in these reactions is accounted for.

$$[Fe_2S_2(NO)_4]^{-2} \rightleftharpoons [Fe_4S_3(NO)_7]^-$$

In the nitrosylation of $Fe_2(SR)_2(CO)_6$, $[Fe_4S_3(NO)_7]^-$ is not obtained since the alkyl group is not labile.

In conclusion two methods of converting carbonyls to nitrosyls have been developed, and the use of nitrite proved to be a good general method. However, the yields obtained in these reactions were less than those obtained by application of the more specific nitric oxide method. This second method is vastly superior, due to the high yields obtainable and the simplicity of workup.

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C_{2h} C_{2v}

Fig. 3.1; The two conformations of $Fe_2(SR)_2(NO)_4$[14,16].

(Fischer projection along Fe-Fe bond)

CHAPTER THREE

N.M.R. EXAMINATION OF $Fe_2(XR)_2(NO)_4$, $Fe_4X_4(NO)_4$ AND $[Fe_4X_3(NO)_7]^-$ (X=S,Se).

3.1 Introduction.

X-ray structural analysis of $Fe_2(SEt)_2(NO)_4$ showed[1] the molecule to be centrosymmetric and of approximately C_{2h} molecular symmetry. There are differences in the literature over the solution phase structure of the compound[2,3]. This structure may be retained as the sole conformer or the solution may contain two components which are presumed to be conformers of C_{2h} and C_{2v} symmetry (fig. 3.1). The results of a solution phase examination of $Fe_2(SR)_2(NO)_4$ by ^1H and ^{13}C n.m.r. spectroscopies are reported in this chapter.

The coordination chemistry of transition metal nitrosyls has been extensively studied and reviewed[4-11]. Nitric oxide possesses a single unpaired electron in an antibonding orbital, which results in it demonstrating considerable versatility in its coordination chemistry. Infra-red nitrosyl stretching frequencies have been used to differentiate between the different types of nitrosyl bonding[5,12,13]. Nitric oxide has a stretching frequency at 1878 cm^{-1}, whilst that of NO^+ in nitrosonium salts is 2200-2300 cm^{-1} [5,12]. NO is bonded in these salts by transfer of the odd electron from NO to the metal, followed by electron pair donation from NO^+. Coordination of NO^+ to transition metals results in a decrease in the NO^+ stretching frequency due to the π back bonding resulting from the overlap of filled d_{π} orbitals

with π^* antibonding orbitals on the ligand. Lewis and coworkers[12] assigned stretching frequencies in the range 1980-1550 cm^{-1} to NO^+ coordinated to transition metals whilst those around 1100 cm^{-1} were assigned to complexes containing NO^-, produced by the transfer of an odd electron from the metal to NO. This classification is not totally satisfactory, and it has been suggested[13] that the frequencies in the range 1500-1700 cm^{-1} are better assigned to NO^-.

X-ray analysis of terminally bonded nitrosyls clearly divide these metal nitrosyls into two classes[7]. The first of these, in which the M-N-O bond is approximately linear, are regarded as complexes containing NO^+. The second group contains M-N-O fragments with a bond angle of around 120^o, and these are assigned to complexes containing NO^-.

With the advent of high field Fourier Transform n.m.r. spectroscopy it has become possible to carry out studies of metal nitrosyls[14-17]. Although only a few metal nitrosyls have been examined by ^{15}N n.m.r. spectroscopy, the ^{15}N chemical shift has been established[15-17] as a simple criterion of structure, readily distinguishing between linear and bent M-N-O fragments. In this chapter the results of solution phase ^{15}N n.m.r. studies of $Fe_2(SR)_2(NO)_4$, $Fe_4X_4(NO)_4$ and $[Fe_4X_3(NO)_7]^-$ (X=S,Se) are reported.

3.2 EXPERIMENTAL.

3.2.1 Materials and instruments.

All chemicals were of reagent grade and were used without further purification. $Na[^{15}NO_2]$ (99% enriched) was purchased from MSD Isotopes Inc., and was used as received. All n.m.r. solvents were of the highest commercial grade available and were dried by conventional methods: deuteriated solvents were of at least 98.5% isotopic purity.

The esters $Fe_2(SR)_2(^{14}NO)_4$ (X=S, R=Me,Et,Pr^n,Pr^i,Bu^t and CH_2Ph; X=Se, R=Me) were prepared either from the carbonyl analogues as described in Chapter 2 or from $Fe_2I_2(NO)_4$ as described by Rauchfuss and Weatherill[3]. ^1H and ^{13}C n.m.r. were recorded for 1% solutions sealed under vacuum, using a Bruker WP-80 and a Varian CFT-20 instrument respectively (the spectra of the benzyl analogue were recorded by Dr. J. McGinnis). The results of ^1H n.m.r. study are recorded in tables 3.1, 3.2 and 3.3 and ^{13}C n.m.r. in table 3.4. It was found that for most solvents that the solubility of $Fe_2(SMe)_2(NO)_4$ was too low for recording of satisfactory ^{13}C n.m.r. spectra.

^{15}N and ^{77}Se n.m.r. spectra were recorded for solutions of $Fe_2(SR)_2(NO)_4$, $Fe_4X_4(NO)_4$ and $[Fe_4X_3(NO)_7]^-$ under nitrogen using the Bruker WH-360 and WP-200 spectrometers at the University of Edinburgh. Spectra were recorded at 36.5 MHz and 68.7 MHz respectively, using $CH_3{}^{15}NO_2$ and Me_2Se as references: it was not found necessary to use any relaxation agents. The results of this ^{15}N

n.m.r. study are recorded in table 3.5.

Infra-red spectra were obtained either as Nujol mulls or KBr discs on a Perkin-Elmer 1330 spectrometer.

3.2.2 Preparation of $[Fe_4S_3(^{15}NO)_7]^-(PPN)^+$ ($PPN^+ = Ph_3PNPPh_3^+$).

$[Fe_4S_3(^{15}NO)_7]^-$ was prepared by an adaption of that given by Brauer[18]. In a typical reaction iron(II) sulphate (5g) in water (25 ml) was added to a mixture of sodium sulphide (5g) and $Na(^{15}NO_2)$ (0.50g) in water (25 ml). The resulting mixture was evaporated to dryness, extracted with acetone and filtered through a 2 cm bed of hyflo to remove finely suspended particles of iron sulphide. The acetone extract was evaporated to dryness to yield a black, amorphous solid, $[Fe_4S_3(^{15}NO)_7]^-Na^+$. The PPN^+ salt was prepared by addition of an equimolar quantity of $[PPN]^+Cl^-$ dissolved in warm water (50 ml) to $[Fe_4S_3(NO)_7]^-$ in water (50 ml). This solution was extracted with CH_2Cl_2 (3 x 50 ml), the organic fraction was dried over Na_2SO_4, filtered, and reduced to small volume. The black product was precipitated by addition of an equal volume of 40/60 petroleum ether, to yield about 0.4g of $[Fe_4S_3(^{15}NO)_7](PPN)$. I.r.: three peaks in the nitrosyl spectrum ca. 1755m, 1695s, and 1658m cm^{-1}. T.l.c.; single spot moving with solvent in acetone and in methanol, non mobile in petrol.

3.2.3 Preparation of $[Fe_4Se_3(^{15}NO)_7]^-(PPN)^+$.

The synthesis of the selenium analogue was by an adaption of that developed by McGinnis[19,20]. $[Fe_4Se_3(^{15}NO)_7]^-$ was prepared as $[Fe_4S_3(^{15}NO)_7]^-$, substituting NaSeH for Na_2S. The initial production of the anionic $[Fe_4Se_3(NO)_7]^-$ was performed under nitrogen to prevent decomposition of the NaSeH, otherwise the production of the selenium analogue was identical to that of the sulphur compound. I.r.: three peaks in the nitrosyl stretching region ca. 1756m, 1690s, and 1658m cm^{-1}. T.l.c.: single spot moving with solvent in acetone and in methanol, non mobile in petrol. Yields in this reaction were comparable to those obtained for the sulphur analogue.

3.2.4 Preparation of $Fe_4S_4(^{15}NO)_4$ from $[Fe_4S_3(NO)_7]^-Na^+$.

The synthesis of $Fe_4S_4(^{15}NO)_4$ was by the method developed by Greenhill-Hooper and Kennedy as part of Senior Honours undergraduate projects.

$[Fe_4S_3(^{15}NO)_7]^-Na^+$ (0.30g) and elemental sulphur (0.50g) were refluxed in toluene (50 ml) for 16 hours under nitrogen. The solvent was evaporated and the product purified by chromatography on a 6 cm x 1 cm (dia.) silica column, eluting with chloroform. Evaporation of the solvent yielded 0.18g of shiny black plates, m.p. 95-97°C. T.l.c.; black spot Rf=0.8 CH_2Cl_2 on silica gel. I.r. single sharp peak at 1756 cm^{-1}. This represents a yield of 72%.

3.2.5 Preparation of $Fe_4Se_4(^{15}NO)_4$ from $[Fe_4Se_3(NO)_7]^-Na^+$.

The synthesis of the selenium analogue of the cubane like cluster was similar to that of its sulphur analogue, substituting grey selenium for sulphur. It was found that the formation of the selenium cubane was slower than that of its sulphur analogue. To remove any unreacted selenium black salt, the solution was washed with water (3 x 50 ml) before evaporating to dryness. The washings were reduced to solid and rereacted with elemental selenium, this procedure was repeated three times. As with its sulphur analogue the selenium cubane analogue forms black plates, in 47% yield. T.l.c. black spot, Rf=0.8 in CH_2Cl_2 on silica gel. I.r. single sharp peak 1756 cm^{-1}.

3.2.6 Preparation of $Fe_2(SR)_2(^{15}NO)_4$ (R = Me, Pr^i).

In a typical reaction $Fe_2(SR)_2(CO)_6$ (1.3 mmol) and $Na[^{15}NO_2]$ (0.50g, 7.1mmol) were refluxed in dry redistilled DMF (30 ml) for 30 minutes under nitrogen, and then cooled to 100°C. Dry redistilled toluene was added (500 ml), causing conversion of green $[Fe(^{15}NO)_2(SMe)_2]^-$ to red $Fe_2(SR)_2(^{15}NO)_4$. This mixture was filtered and the filtrate evaporated to dryness: the residue was dissolved in CH_2Cl_2 (40 ml) and the solution washed with water (10 x 300 ml). The organic fraction was dried over Na_2SO_4, filtered, and reduced to small volume. The dark red product was precipitated by addition of an equal volume of ice-cold methanol. The resulting compounds were identified

by comparative ^{1}H n.m.r: 2.8p.p.m. (doublet) in $CDCl_3$. I.r.:1775(w), 1740s, and 1718m cm^{-1}. The average yield for this reaction was 25%.

3.2.7 The infra-red spectra of N-15 labelled iron-nitrosyls.

The ^{14}NO absorption frequencies have been recorded for $Fe_2(SR)_2(NO)_4$, $[Fe_4X_3(NO)_7]^-$ and $Fe_4X_4(NO)_4$ (X=S,Se) by several workers[12,19-24]. As part of the study of the ^{15}N analogues of these complexes their i.r. spectra were recorded for the nitrosyl stretching frequencies (table 3.6). An increase in the mass of atoms undergoing oscillation leads to a decrease in the observed frequency. The position of the ^{15}N bands were calculated by treating the NO group as isolated from the rest of the complex by applying the formula for isotopic shifts in diatomic molecules[25];

$$\nu^{i}_{osc}/\nu_{osc} = \sqrt{\mu/\mu^{i}}$$

where ν_{osc} is the absorption frequency and μ the reduced mass: the subscript 'i' referring to the ^{15}N isotopic species.

Table 3.6: I.r. data for the ^{14}N and the ^{15}N isotopic absorptions for ν(N-O).

Compound	$\nu(^{14}N\text{-}O)/cm^{-1}$	$\nu(^{15}N\text{-}O)/cm^{-1}$
$Fe_2(SMe)_2(NO)_4$	1810w	1775w
	1775s	1740s
	1750m	1718m
$[Fe_4S_3(NO)_7]^-$	1790m	1755m

	1720s	1695s
	1690m	1658m
$[Fe_4Se_3(NO)_7]^-$	1790m	1756m
	1720s	1690s
	1690m	1658m
$Fe_4S_4(NO)_4$	1790s	1756s
$Fe_4Se_4(NO)_4$	1790s	1756s

The observed frequencies agree well with those calculated from the ^{14}N values, variations being of the same order as those observed by McGinnis between the ^{12}C and ^{13}C analogues of sodium nitroprusside[19].

3.3 Results and Discussion.

3.3.1 ^1H and ^{13}C n.m.r study of $Fe_2(XR)_2(NO)_4$ (X = S,Se).

In this section the results of ^1H and ^{13}C n.m.r. studies of $Fe_2(XR)_2(NO)_4$ are reported, including observation of solvent-induced shift phenomena and the study of a dynamic intramolecular isomerisation process.

Table 3.1: Solvent dependence of n,m,r, parameters of $Fe_2(SMe)_2(NO)_4$

Solvent	$\delta(^1H)$/p.p.m.[a]	$\Delta\nu$/Hz	T_c/K	$\Delta G^{\ddagger}$/kJ mol^{-1}
Toluene-d_8	2.20	5.8	357	78.3
Benzene-d_6	2.35	4.9	353	77.9
C_6H_5Cl	2.42	3.1	b	
C_6H_5Br	2.45	3.2	b	
C_6H_5I	2.49	3.3	b	
$C_6D_5NO_2$	2.52	1.2	352	77.0
o-$C_6H_4Cl_2$	2.60	4.0	b	
Pyridine	2.72[c,d]	d	-	
$CCl_2=CCl_2$	2.75	2.0	e	
$(CCl_2=CCl)_2$	2.76	2.0	e	
CCl_4	2.76	2.0	e	
CD_2Cl_2	2.77	1.2	339	78.7
Cyclohexane-d_{12}	2.78	1.7	344	78.9
$CDCl_3$	2.83	1.6	e	
CD_3NO_2	2.83	f	f	
CD_3CN	2.89	1.3	291	67.0
C_6F_6	2.92	f	f	
Acetone-d_6	2.92	1.2	284	65.5
Dioxan-d_8	2.95	1.6	343	78.8
THF-d_8	3.02	1.0	330	77.0
DMSO-d_6	3.31[c,g]	g	-	
DMF-d_7	3.54[c,h]	c	h	

Footnotes to Table 3.1

a/ Mean chemical shift of C_{2h} and C_{2v} isomers, measured at 308 K.

b/ Not studied.

c/ Broad, unresolved absorption.

d/ Mono-nuclear complex, $[Fe(NO)_2(pyridine)]^+$ detected by e.p.r. spectroscopy.

e/ No coalescence observed even at boiling point of solvent.

f/ No resolution of $\Delta\nu$, even at freezing point of solvent.

g/ Mono-nuclear complex, probably $[Fe(NO)_2(SMe)(DMSO)]$, detected by e.p.r. spectroscopy.

h/ At elevated temperatures yields the mono-nuclear complexes $[Fe(SMe)(NO)_2(DMF)]$ and $[Fe(NO)_2(DMF)_2]^+$ (Ref. 3).

^1H spectra were recorded for $Fe_2(SMe)_2(NO)_4$ in twenty-two solvents (table 3.1). For solutions in DMSO-d_6, DMF-d_7 and pyridine it was apparent that paramagnetic species were present whose structures are discussed in Chapter 4. Solutions in benzonitrile and benzaldehyde consistently underwent major decompositions to yield MeS^-. On four separate attempts to prepare a solution in methanol-d_4 the tube exploded; hence no attempts were made to record spectra in other alcohols.

The ^1H chemical shifts observed can be divided into three groups. The first of these demonstrates chemical shifts in the range 2.75 - 2.83 p.p.m. and is composed of chlorinated hydrocarbons and cyclohexane. These are all low polarity solvents with low polarizability and the spectra obtained can be regarded as those for a solvent uncoordinated to $Fe_2(SR)_2(NO)_4$. These solvents are termed 'inert solvents'[26].

The second group of solvents demonstrate a change in the proton chemical shifts to high field, in the range 2.2 - 2.7 p.p.m. (except hexafluorobenzene at 2.92 p.p.m.), these are composed of aromatic solvents and demonstrate Aromatic-Solvent Induced Shifts (ASIS). Since its discovery[27], ASIS has been the subject of much investigation. However, there is no generally accepted interpretation of this phenomenon. Explanations include dipole-induced dipole interactions[27], specific solute-solvent orientations to yield 1:1 complexes[28], dynamic 1:n complexes[29] and dipole-quadrupole interactions[30].

Table 3.2: N.m.r. assignments for $Fe_2(SR)_2(NO)_4$[a]

Compound	Solvent	$\delta(^1H)$/p.p.m.	$\Delta G^{\ddagger}$/kJ mol^{-1}	Assignment
$Fe_2(SMe)_2(NO)_4$	$CDCl_3$	2.83	78.3(4)	CH_3
	$C_6D_5CD_3$	2.16, 2.23		CH_3
$Fe_2(SEt)_2(NO)_4$	$CDCl_3$	1.53, 1.58		CH_3
		3.07, 3.10		CH_2
	$C_6D_5CD_3$	1.13, 1.16	75.6(5)	CH_3
		2.53, 2.63	75.8(4)	CH_2
$Fe_2(SPr^n)_2(NO)_4$	$CDCl_3$	1.11		CH_3
		1.96		$CH_3CH_2CH_2$
		3.02, 3.05	75.5(5)	$CH_3CH_2CH_2$
	$C_6D_5CH_3$	0.84		CH_3
		1.61		$CH_3CH_2CH_2$
		2.64, 2.68		$CH_3CH_2CH_2$
$Fe_2(SPr^i)_2(NO)_4$	$CDCl_3$	1.54, 1.57		CH_3
		3.04, 3.07		CH
	$C_6D_5CD_3$	1.26[b]		CH_3
		2.69[b]	59.3(6)	CH
$Fe_2(SBu^t)_2(NO)_4$	$CDCl_3$	1.45		CH_3
		-		Me_3C
	$C_6D_5CD_3$	1.23[c]		CH_3
		-		Me_3C
$Fe_2(SCH_2Ph)_2(NO)_3$	$CDCl_3$	4.18, 4.22		CH_2
		7.43		Ph
	$C_6D_5CD_3$	3.82, 3.85	76.8(5)	CH_2
		7.07		Ph

a. Data at 308 K, chemical shift in p.p.m. from Me_4Si.

b. $\delta(^1H)$ at 233 K: 1.23, 1.27, 2.47 p.p.m.

c. No splitting observed even at 223 K.

The interpretation based upon dipole-quadrupole interactions[27], involves a theoretical approach which depends upon the solute possessing a permanent dipole moment. This permanent dipole is postulated to induce the solute-solvent interaction leading to ASIS, and hence, if a permanent dipole is absent, ASIS will not occur. $Fe_2(SMe)_2(NO)_4$, exists as a dynamic equimolar mixture of C_{2h} and C_{2v} conformational isomers in solution (see below). The C_{2v} isomer possesses a dipole moment, however, the C_{2h} conformation possesses genuine C_{2h} symmetry and therefore cannot possess a permanent dipole moment. Comparison of the chemical shifts for the two isomers (table 3.1) shows them both to demonstrate similar ASIS. This is also true for other alkyl substituted isomers of $Fe_2(SR)_2(NO)_4$ in toluene (table 3.2) and for $Fe_2(SeMe)_2(NO)_4$ (table 3.3). These results thus question the validity of this particular explanation of ASIS.

The observed direction of shift of the ^1H chemical shifts by ASIS to high field in comparison with 'inert solvents' is in the same direction as that observed for ^1H resonances in organic molecules[31]. The magnitude of this shift varies between different aromatic solvents. The induced shift of benzene is less than that observed in toluene by 0.15 p.p.m.. It has been shown that toluene is a better electron donor than benzene[32], whilst halogen substituted benzenes are less efficient donors[33]. This is due to the relative electronegativities of the ring substituents in comparison to hydrogen[34]. Substituted alkyl groups are electron donating, whilst groups such as halogens are electron withdrawing[35,36]. Hence, the more electron withdrawing substituents on the benzene ring the weaker

the interaction and observed shifts. The ASIS listed in table 3.1 for substituted benzenes is entirely consistent with their acting as electron doners or acceptors towards the solute $Fe_2(SMe)_2(NO)_4$.

In table 3.2 the results of a ^1H and a ^{13}C n.m.r. study of $Fe_2(SR)_2(NO)_4$ (R=Me, Et, Pr^n, Pr^i, Bu^t and $PhCH_2$) in both $CDCl_3$ and toluene-d_8 are listed. The ^1H chemical shifts show a significant shift to high field on changing from $CDCl_3$ to toluene-d_8, but the corresponding solvent induced shift in the ^{13}C resonances appears modest in comparison.

The magnitudes of the observed ASIS in the ^1H spectra are dependent on both the alkyl chain length and also the position on the chain itself. The solvent induced shift for the methyl derivative is ca. 0.6 p.p.m., whilst for the ethyl derivative is ca. 0.4 p.p.m. for the methyl protons and ca. 0.5 p.p.m. for the methylene protons. Extension of the chain length by a second methylene group, forming the n-propyl analogue again causes a decrease in the solvent induced shifts observed. As in the ethyl derivative, the magnitude of the ASIS is greatest for the S-methylene protons ca. 0.38 p.p.m.. The methylene protons of the Me-C carbon demonstrate ASIS ca. 0.35 p.p.m. and the methyl protons ca. 0.27 p.p.m.. This trend of decreasing shifts appears to be a characteristic of this type of compound since we have observed a similar effect in the isoelectronic carbonyl analogues (cf. appendix 2). In the ^{13}C n.m.r. spectra for the methyl and ethyl derivatives of $Fe_2(SR)_2(NO)_4$ the corresponding shifts are ca. 0.30, 0.15 and 0.05 p.p.m. respectively, the magnitude of these solvent shifts being relatively modest in

comparison with those observed in the ^{1}H spectra. An examination of $Fe_2(SMe)_2(NO)_4$ by ^{13}C n.m.r. spectroscopy in various solvent was attempted. This study was greatly hampered by the low solubility of the solute in the majority of solvents examined. However, the observed shifts were found, as with toluene, to be modest when compared to those observed in the proton spectra.

The results of this study are qualitatively consistent explanations for the ASIS phenomenon based upon either 1:1 charge-transfer complexes or 1:n dynamic complexes, but are not consistent with models based upon the existence of a permanent dipole moment in the solute.

The third group of solvents demonstrate a shift in the ^{1}H chemical shift to low field, in the range 2.8 - 3.0 p.p.m.. These (with the exception of hexafluorobenzene) are strongly polar and strongly electron-donating solvents. All the solvents in this group are non-protonic, non-polychlorinated aliphatic solvents which possess a single dominant bond dipole and as such conform to Taft's criteria for 'select solvents'[37-39]. Several quantitative scales of solvent properties have been derived for this effect, these include measures of solvent acidity[40], or basicity[41], or dipolarity[42], or acceptor number[43], or even the 'chromatographic strength'[44]. All these quantitative scales are linear with Taft's solvatochromic parameter π^* [37-39] and as such are therefore measures of the solvent dipolarity/polarizability rather than any acid/base phenomena[45]. The ^{1}H chemical shifts listed in table 3.1 correlate reasonably well with π^* for the group of solvents examined. The chemical shifts observed

Table 3.3: Solvent dependence of n.m.r. parameters of $Fe_2(SeMe)_2(NO)_4$

Solvent	$\delta(^1H)$/p.p.m.[a]	$\Delta\nu$/Hz
Toluene-d_8	2.20	7.2
Benzene-d_6	2.38	6.4
$CDC\ell_3$	2.83	3.4
$CD_2C\ell_2$	2.84	3.2
Acetone-d_6	2.95	1.7
DMSO-d_6	3.35	b

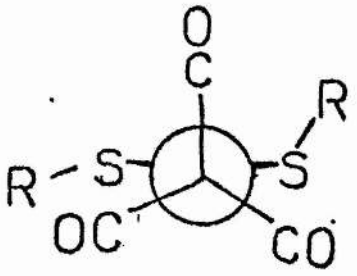
a/ Mean chemical shift of C_{2h} and C_{2v} isomers, measured at 308 K.

b/ No resolution of $\Delta\nu$, even at freezing point of solvent; paramagnetic mono-nuclear complex, probably $[Fe(NO)_2(SeMe)(DMSO)]$, detected by e.p.r. spectroscopy.

for this group of solvents can therefore be assumed to be due to properties intrinsic to the solvents themselves and do not necessarily depend upon any donor-acceptor interactions between the solute and solvent[45].

In conjunction with this study, ^{1}H n.m.r. spectra were recorded for $Fe_2(SeMe)_2(NO)_4$ in a very limited range of solvents (table 3.3). The chemical shifts obtained are little different from those observed for the sulphur analogue. However, the magnitude of the isomer shifts recorded for the selenium analogue are between 0.5 and 2.0 Hz larger.

X-Ray structural analysis of $Fe_2(SEt)_2(NO)_4$ has shown the compound to exist as a single structural conformer[1], that of C_{2h} (fig. 3.1) in the solid state. In this conformation the methyl ester $Fe_2(SMe)_2(NO)_4$ possesses both a single proton and carbon environment and hence if this single conformation is retained on dissolution a single peak would be observed in both the ^{1}H and ^{13}C n.m.r. spectra. However, at ambient spectrometer temperature (308 K), a 1:1 doublet is observed in the majority of solvents examined, both in the ^{1}H and ^{13}C n.m.r. spectra, tables 3.1 and 3.2. This observation agrees with that of Rauchfuss and Weatherill[3] who ascribed this observation to the coexistence of both the C_{2h} and the C_{2v} (fig. 3.1) conformers in solution.



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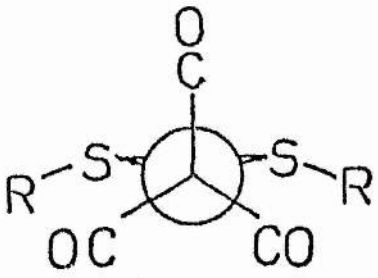

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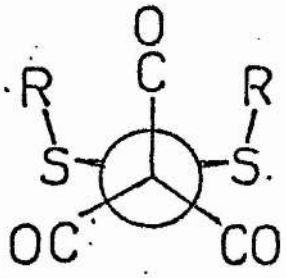

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Fig. 3.2; conformations of $Fe_2(SR)_2(CO)_6$.

(Fischer projection along Fe-Fe bond)

$Fe_2(SR)_2(CO)_6$, isoelectronic with $Fe_2(SR)_2(NO)_4$ exists as two chromatographically isolable conformational isomers[46,47] (fig. 3.2). Solution phase examination of the isolated isomers has shown them to be readily interconvertible[47]. The rate of conversion being dependent on both temperature and the degree of substitution of the C-S carbon of the alkyl chain. The greater the degree of substitution the faster the rate of interconversion, indeed the t-butyl analogue has been demonstrated to be fluxional on the n.m.r. time scale. The process of isomerisation in these alkyl esters of $Fe_2(SR)_2(CO)_6$ is by the relatively common process in chalcogen substituted cluster compounds of torsion barrier inversion[48].

The two environments observed in the n.m.r. spectra of $Fe_2(SMe)_2(NO)_4$ and its alkyl analogues have been ascribed to the mutual coexistence of both the C_{2h} and C_{2v} isomers in solution[3]. Examination of the structure of the C_{2v} isomer of $Fe_2(SMe)_2(NO)_4$ shows it to possess like the C_{2h} isomer a single proton and carbon environment. The environment of these alkyl ligands in the two conformers are slightly different and hence should demonstrate different chemical shifts. In the isoelectronic carbonyl analogues, isomer shifts of up to 0.50 and 13.3 p.p.m. have been observed in the ^1H and ^{13}C n.m.r. spectra respectively[20]. These isomer shifts are much larger than the shifts observed for $Fe_2(SR)_2(NO)_4$. This suggests that the difference between the two environments of the alkyl groups in the nitrosyl complexes is less than that in the carbonyls. The Fe_2S_2 ring in the carbonyl complexes is puckered[49], whereas in the nitrosyl it is a planar rhombus[1]. The sulphur atoms in the nitrosyls

Table 3.4 N.m.r. assignments for $Fe_2(SR)_2(NO)_4$[a]

Compound	Solvent	$\delta(^{13}C)$/p.p.m.	Assignment
$Fe_2(SMe)_2(NO)_4$	$CDCl_3$	27.45	CH_3
	$C_6D_5CD_3$	26.95, 27.18	CH_3
$Fe_2(SEt)_2(NO)_4$	$CDCl_3$	19.14	CH_3
		39.45, 40.15	CH_2
	$C_6D_5CD_3$	18.98	CH_3
		39.49, 40.19	CH_2
$Fe_2(SPr^n)_2(NO)_4$	$CDCl_3$	13.11	CH_3
		27.33	$CH_3\mathit{CH_2}CH_2$
		47.33, 47.66	$CH_3CH_2\mathit{CH_2}$
	$C_6D_5CH_3$	12.93	CH_3
		27.50	$CH_3\mathit{CH_2}CH_2$
		47.48, 47.91	$CH_3CH_2\mathit{CH_2}$
$Fe_2(SPr^i)_2(NO)_4$	$CDCl_3$	27.64	CH_3
		49.70, 50.63	CH
	$C_6D_5CD_3$	27.47	CH_3
		49.94, 50.92	CH
$Fe_2(SBu^t)_2(NO)_4$	$CDCl_3$	34.14	CH_3
		52.95	$Me_3\mathit{C}$
	$C_6D_5CD_3$	33.96	CH_3
		57.05	$Me_3\mathit{C}$
$Fe_2(SCH_2Ph)_2(NO)_3$	$CDCl_3$	48.63, 49.37	CH_2
		128.2, 129.1	Ph
	$C_6D_5CD_3$	d	CH_2
		d	Ph

a. Data at 308 K, chemical shift in p.p.m. from Me_4Si.

d. Not studied.

are hence further apart than in the carbonyls and it would seem reasonable that the S-alkyl groups would have less effect on each other.

Fe_2S_2 ring fission can be disregarded as a possibility for the existence of the two environments generated in the solution phase since the individual iron atoms possess formal oxidation states of $-1(d^9)$ with one unpaired electron[1]. The nitrosyl complexes, like those of the carbonyls, are diamagnetic due to the existence of an Fe-Fe bond[1,49,50]. If a monomerisation process were to occur, then the resultant mixture would be observed to be paramagnetic. Solution phase examination of $Fe_2(SMe)_2(NO)_4$ in toluene, chloroform and THF, unlike those in DMF, DMSO and pyridine, yielded no detectable paramagnetic species by e.p.r. spectroscopy (cf. chapter 4). Thus fission of the Fe_2S_2 ring to yield paramagnetic complexes can be disregarded as a reason for the generation of more than one proton and carbon environment for $Fe_2(SMe)_2(NO)_4$ in these solutions. Likewise a displacement of RS^- from the Fe_2S_2 ring is unlikely since the resulting peaks in the spectra would be to high field of those observed.

Variable temperature (V.T.) ^1H n.m.r. spectra were recorded for $Fe_2(SR)_2(NO)_4$ (R = Me, Et, Pr^n, Pr^i, Bu^t and $PhCH_2$) in toluene-d_8 (table 3.2). For all of these except the t-butyl analogue, spectra were obtained at low temperatures consistent with the existence of two isomeric forms. On raising the temperature the observed spectra were replaced with those consistent with the existence of a single isomeric form. This process was reversed on reducing the temperature,

the original spectra being regained unchanged. These observations agree with the existence of a $C_{2v} \rightleftharpoons C_{2h}$ isomerisation process for the methyl, ethyl, n-propyl, i-propyl, and benzyl analogues. At low temperatures both isomers can be detected but, as the temperature is increased, the rate of isomerisation surpasses that of detection for the individual isomeric forms, resulting in the observation of averaged spectra.

The activation energies $\Delta G^{\ddagger}$ were calculated by the approximate method given by Abraham and Loftus[51] from the isomer shift $\Delta \nu$ and T_c. The results of these energy barrier calculations for the $C_{2v} \rightleftharpoons C_{2h}$ isomerisation process are listed in table 3.2. Comparison of the activation energy ($\Delta G^{\ddagger}$) for the isomerisation process show that an increase in the degree of substitution on the C-S carbon results in a decrease in the energy required for the isomerisation process, this is consistent with that observed for the carbonyl analogues[47].

Turning to the details of the energies listed in table 3.2. Replacement of one hydrogen in the methyl compound by an alkyl group to give either the ethyl or the n-propyl derivative causes a decrease in $\Delta G^{\ddagger}$ of about 2.5 KJ mol^{-1}. Replacement of a second hydrogen to give the i-propyl compound causes a decrease by a further 17 KJ mol^{-1}. Replacement of the third hydrogen to yield the t-butyl ester resulted in the detection of no resolvable splitting even at 223 K. This may be the consequence of either the existence of only the C_{2h} isomer in solution due to steric effects or because the activation energy is less than that detectable (due to the freezing of the solvent). If both isomers exist in solution, then for reasonable

values of ΔV, an upper limit for $\Delta G^{\ddagger}$ of about 50 KJ mol^{-1} may be assigned.

For the ethyl ester the values for ΔV varies from ca. 2.0 Hz for the methyl to ca. 6.9 Hz for the methylene protons. For both sets of protons, distinct values for T_c were determined which enabled the calculation of ΔG at two different temperatures. The variation of $\Delta G^{\ddagger}$ with temperature depends on changes in entropy $\Delta S^{\ddagger}$ $(\partial \Delta G/\partial T = -\Delta S)$. The entropies of the two isomers must be very similar and although the nature of the transition state is not known it is very unlikely that its entropy will be greatly different. Hence $\Delta S^{\ddagger}$ will be very small and $\Delta G^{\ddagger}$ should be relatively temperature independent. This is verified by the calculated $\Delta G^{\ddagger}$ values for the ethyl analogue which remain identical within experimental error over a 16 K temperature variation.

$Fe_2(SMe)_2(NO)_4$ was examined by V.T. ^1H n.m.r. in a limited number of solvents(table 3.1). These included examples from each of the three groups of solvents described earlier. T_c for the $C_{2v} \rightleftharpoons C_{2h}$ equilibrium for solutions in toluene-d_8, benzene-d_6, nitrobenzene-d_5, CD_2Cl_2, cyclohexane-d_{12}, CD_3CN, acetone-d_6, dioxan-d_8 and THF-d_8 were calculated from which values of $\Delta G^{\ddagger}$ were determined (table 3.1). Values of $\Delta G^{\ddagger}$ for these solvents, except for CD_3CN and acetone-d_6 are essentially identical with a value of 78 ± 1 KJ mol^{-1}, and can be taken as constant and thus independent of solvent. In both CD_3CN and acetone-d_6 the value of $\Delta G^{\ddagger}$ is 11-13 KJ mol^{-1} lower. The existence of a solvent-solute interaction is apparent in these two solutions which results in a significant reduction in the energy required for the

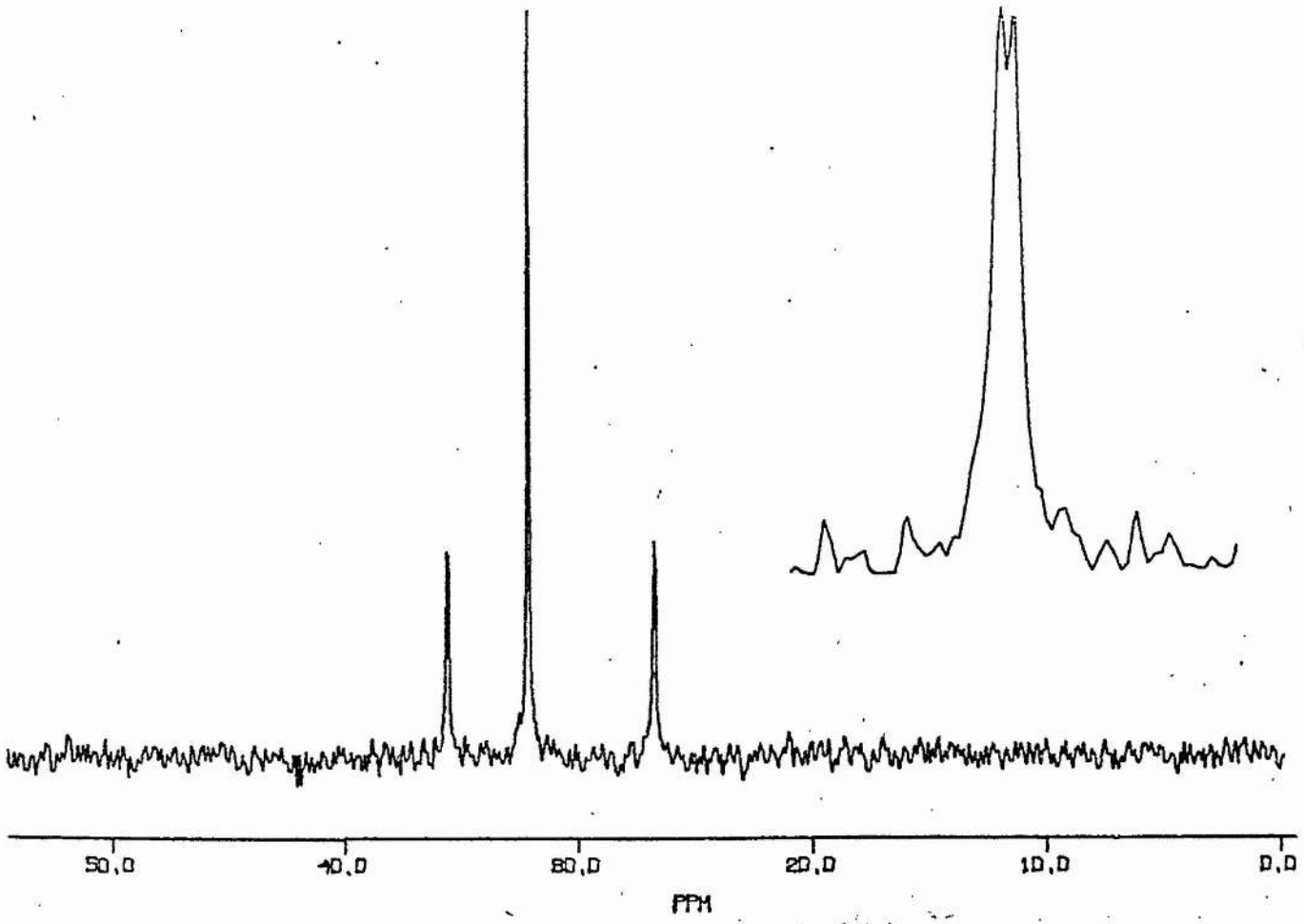

Fig. 3.3; ^{15}N n.m.r. spectrum of $Fe_2(SPr^i)_2(NO)_4$.

torsion barrier inversion. E.p.r. examination of freshly prepared solutions in either CD_3CN or acetone-d_6 showed no evidence for the presence of paramagnetic species.

In conjunction with this V.T. ^1H n.m.r. examination of $Fe_2(SMe)_2(NO)_4$ the selenium analogue was examined in toluene-d_8, benzene-d_6, $CDCl_3$, CD_2Cl_2, acetone-d_6 and DMSO-d_6. In all solvents other than DMSO no coalescence was observed at temperatures up to, or indeed somewhat above, the boiling points of the solvents. For $Fe_2(SMe)_2(NO)_4$ the value for $\Delta G^{\ddagger}$ was essentially constant at 78 KJ mol^{-1} whether the solvent was benzene, toluene or CD_2Cl_2: assuming that this constancy is true also for the selenium analogue, then a lower limit for the $\Delta G^{\ddagger}$ for the $C_{2h} \rightleftharpoons C_{2v}$ equilibrium in $Fe_2(SeMe)_2(NO)_4$ is estimated to be at least 86 KJ mol^{-1}. This is notably higher than that observed for the sulphur analogue.

3.3.2 ^{15}N N.M.R. examination of $Fe_2(SR)_2(NO)_4$, $Fe_4X_4(NO)_4$ and $[Fe_4X_3(NO)_7]^-$ (X=S,Se).

The ^{15}N n.m.r. spectra recorded for $Fe_2(SMe)_2(NO)_4$ and $Fe_2(SPr^i)_2(NO)_4$ (in toluene at ambient spectrometer temperature:308K) showed the presence of an intense singlet and a pair of doublets (table 3.5, fig. 3.3). The intense singlet can be assigned to the C_{2h} conformer and the pair of doublets to the C_{2v} conformer. In the C_{2h} conformation all of the nitrosyls ligands are equivalent. This is

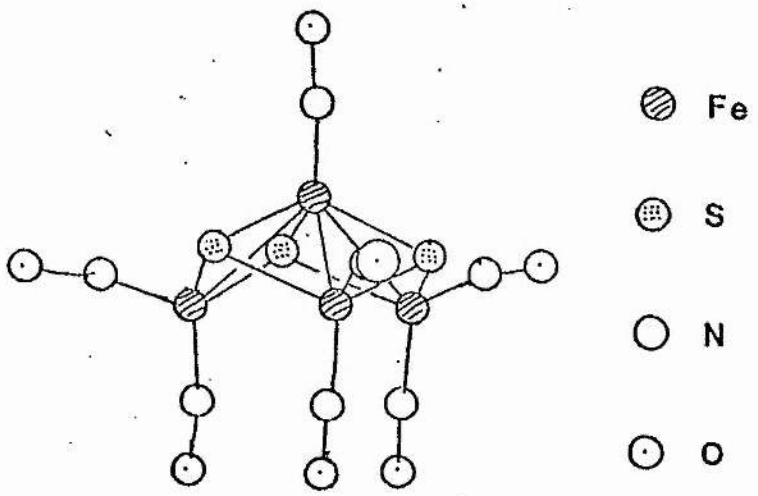

Fig. 3.4; Structure of $[Fe_4S_3(NO)_7]^-$ [52]

not so for the C_{2v} conformer, where although the two alkyl groups and the two iron atoms are equivalent, the two nitrosyls in each $Fe(NO)_2$ fragment are non-equivalent. Homonuclear spin-spin coupling $^2J(^{15}NFe^{15}N)$ between the two ^{15}N nuclei results in the observation of an AX spectrum (long range $^3J(^{15}NFeFe^{15}N)$ was not detected). Intergration of the spectrum for both $Fe_2(SPr^i)_2(NO)_4$ and $Fe_2(SMe)_2(NO)_4$ showed the presence of an equimolar mixture of the two conformers, this is consistent with ^1H and ^{13}C evidence.

In the ^1H and ^{13}C n.m.r. section above a study of the $C_{2h} \rightleftharpoons C_{2v}$ isomerisation process by V.T. n.m.r. is reported. As with the ^1H and the ^{13}C n.m.r. spectra the ^{15}N n.m.r. spectra should be temperature dependent, at high temperatures the rate of isomerisation becoming too fast for detection of the individual nitrogen environments, resulting in the nitrosyl ligands appearing to exist in a single averaged environment. V.T. examination of $Fe_2(SPr^i)_2(NO)_4$ up to 310K (chosen because of its lower activation energy ΔG^*), had no effect on the observed spectra. Raising the temperature further resulted in the decomposition of the compound.

The ^{15}N chemical shifts observed are in the region characteristic[15-17] of linear M-N-O groups, in agreement with the crystal structure of $Fe_2(SEt)_2(NO)_4$[1]. The ^{15}N n.m.r. results confirm the existence of the C_{2h} and C_{2v} isomers in solution which were inferred from ^1H and ^{13}C n.m.r. evidence.

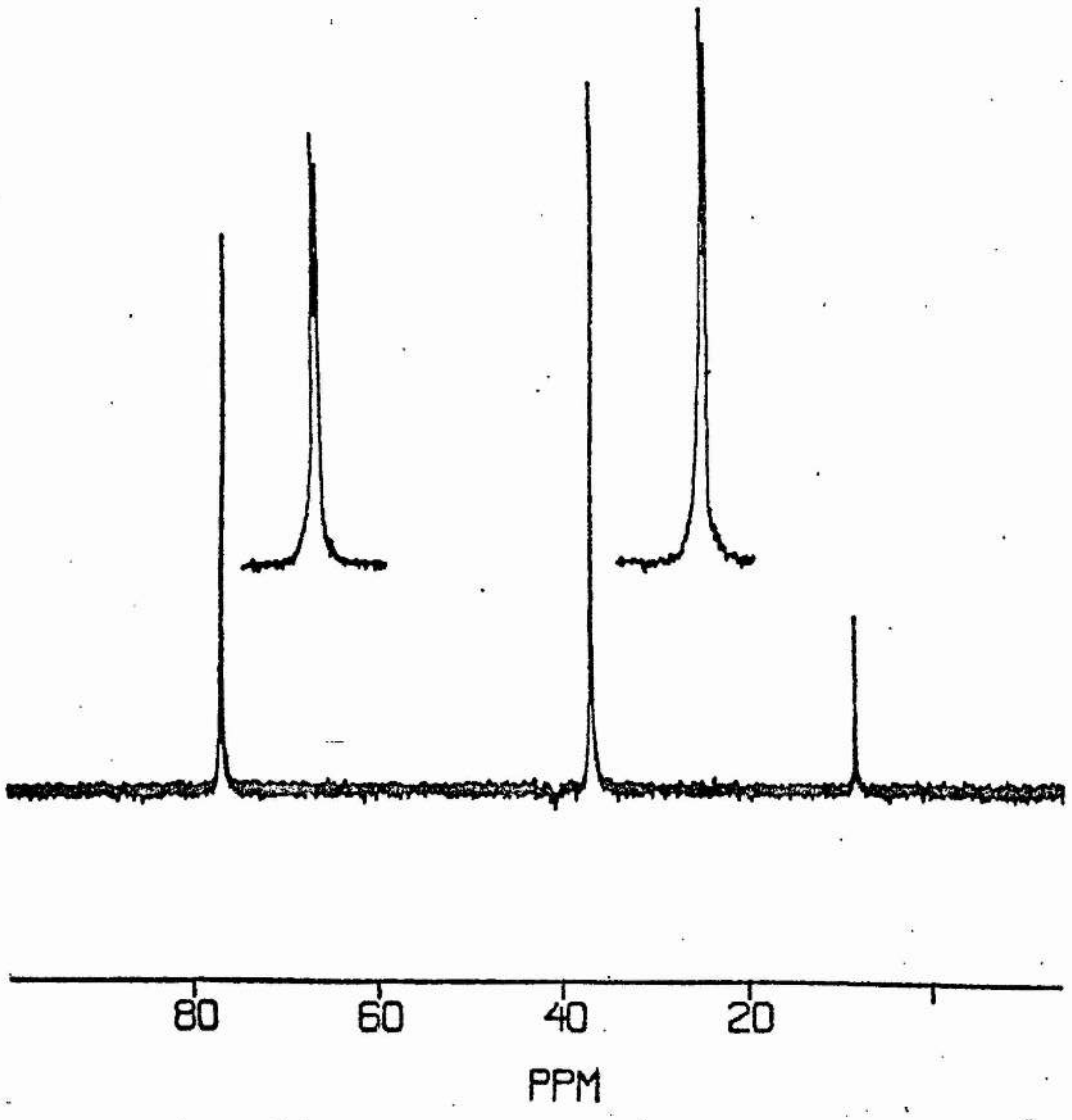

Fig. 3.5; ^{15}N n.m.r. spectrum of $[Fe_4S_3(NO)_7]^-$.

The X-ray structure of the cubane analogues $Fe_4X_4(NO)_4$ (X = S,Se) is known[21,22] and consists of a tetrahedron of iron atoms with a chalcogen atom resting on each face. A nitrosyl ligand is terminally bonded to each iron atom, the M-N-O bond being essentially linear. ^{15}N n.m.r.examination of the two analogues in CD_2Cl_2 gave a single peak (table 3.5) in the region assigned to linear M-N-O bond[15-17]. The X-ray structure of $[Fe_4S_3(NO)_7]^-$ is known[52] (fig. 3.4) and has overall C_{3v} symmetry and possesses three nitrosyl environments in relative abundances 1:3:3. The unique apical iron bears a single nitrosyl ligand, whilst each of the three basal iron atoms bear two, one which may be described as axial and the other equatorial. Examination of the ion by ^{15}N n.m.r. spectroscopy in CD_2Cl_2 revealed a spectra composed of three peaks (table 3.5, fig. 3.5), in relative intensity 1:3:3. The first of these peaks is due to the unique apical nitrosyl, the close similarity between the apical site and the corner of one of the cubane analogues is demonstrated by the very similar ^{15}N chemical shift. The other two peaks are due to the two nitrosyl environments present in the three $Fe(NO)_2$ fragments. However, at present it is not possible to discern which environment relates to which peak. In addition $^2J(^{15}N\ Fe\ ^{15}N)$ coupling is observed for the nitrosyls in the $Fe(NO)_2$ fragments, observed as a doublet, with similar splitting to that observed in $Fe_2(SR)_2(NO)_4$.

Examination of $[Fe_4Se_3(NO)_7]^-$ yielded a similar spectrum to its sulphur analogue. In the examination of $[Fe_4Se_3(NO)_7]^-$ and of $Fe_4Se_4(NO)_4$ no short range coupling to ^{77}Se was resolved. Although the selenium analogue has been prepared previously[19,20,22], its

Table 3.5: ^{15}N n.m.r. data for iron-chalcogen-nitrosyl cluster compounds.

Compound		$\delta(^{15}N)$/p.p.m.[a]		
$Fe_2(SMe)_2(NO)_4$	(C_{2h})	+30.5 (s)		
$Fe_2(SMe)_2(NO)_4$	(C_{2v})	+23.1 (d)	J=2.8 Hz	
		+36.2 (d)		
$Fe_2(SPr^i)_2(NO)_4$	(C_{2h})	+30.2 (s)		
$Fe_2(SPr^i)_2(NO)_4$	(C_{2v})	+26.7 (d)	J=2.6 Hz	
		+35.7 (d)		
$(PPN)^+[Fe_4S_3(NO)_7]^-$	[b]	+ 7.7 (s)	+36.0 (d, J=4.3 Hz)	+76.1 (d, J=4.3 Hz)
$(PPN)^+[Fe_4Se_3(NO)_7]^-$	[b,c]	+ 7.8 (s)	+29.5 (d, J=4.1 Hz)	+74.9 (d, J=4.1 Hz)
$Fe_4S_4(NO)_4$		+12.8 (s)		
$Fe_4Se_4(NO)_4$	[c]	+20.5 (s)		

a. Chemical shifts in p.p.m., referenced against $CH_3{}^{15}NO_2$ as external reference for samples enriched to 99% ^{15}N. Spectra recorded on samples in $CDCl_3$ solution at 298K; all observed couplings are $^2J(^{15}N\ Fe\ ^{15}N)$.

b. The PPN^+ cation contained natural abundance ^{15}N.

c. No coupling of ^{15}N to ^{77}N was detected.

structure has never been definetively established, other than by inference. This examination provides proof of structure. The ^{77}Se n.m.r. was recorded for $[Fe_4Se_3(NO)_7]^-$. The resulting spectrum was composed of a singlet (ca. 1468.0 p.p.m., ref. Me_2Se) with no resolved coupling to nitrogen.

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CHAPTER FOUR.

FORMATION OF PARAMAGNETIC MONONUCLEAR IRON-NITROSYL COMPLEXES FROM DIAMAGNETIC $Fe_2(SR)_2(NO)_4$: CHARACTERISATION BY E.P.R. SPECTROSCOPY AND STUDY OF THIOLATE EXCHANGE REACTIONS.

4.1 Introduction.

McDonald and coworkers[1] first demonstrated in 1965 that aqueous solutions of iron(II) salts react with nitric oxide in the presence of mercaptans or phosphates to generate paramagnetic species with four coordinate geometry of general stoichiometry $[Fe(NO)_2L_2]^+$, characterised by their isotropic e.p.r. spectra with g-centre ca. 2.03. More recently it has been shown that iron(II) salts will react in the presence of nitric oxide with halides and pseudohalides[2], alcohols and alkoxides[3], mercaptides[4,5] and mercapto-purines and mercapto-pyrimidines[6] to form similar species. In all cases[2-6] the observed spectra possessed g-centres ca. 2.03, except in the case of bromide and iodide when the centre was shifted to high field. The g-value is the proportionality constant (for a system with S=1/2 and I=0) in the equation $h\nu=g\mu_B B$; where ν is the the fixed frequency of the microwave radiation and B the magnitude of the static field at resonance. For a free electron g=2.0023: this is termed the 'free spin' or 'spin only' value. The g-value is a unique property of the paramagnetic species and is independent of any electron-nuclear hyperfine interactions that may be present. In general, g is anisotropic, having three principal components. This anisotropy is normally only detected in solid phase examinations, while isotropic

spectra are obtained, because of rapid tumbling, in solution phase examinations. The magnitude of deviation from 2.0023 depends on the nature of the spin-orbit coupling. For transition-metal complexes the central metal atom is usually the major source of these g-shifts. Thus g-centres have been used for the tentative assignments of unresolved e.p.r. spectra[7-10].

The iron atoms in $Fe_2(SR)_2(NO)_4$ have been assigned a formal oxidation state of $-1(d^9)$[11] each possessing one unpaired electron. This would cause the compounds to be paramagnetic but for the existence of an iron-iron bond. In chapter 3, it was reported that, in an n.m.r. study of the diamagnetic compound $Fe_2(SR)_2(NO)_4$ the Fe-S ring remains intact on dissolution in non-polar solvents. However, it was found that in polar solvents, such as DMF, broad unresolved spectra were obtained. This was explained as being due to the presence of mono-iron fragments resulting from the fission of the iron-sulphur ring. The proposed structure for the mono-iron complexes[1] $[Fe(NO)_2L_2]^-$ is closely related to that of the neutral diamagnetic complex $Fe_2(SR)_2(NO)_4$[12,13]. In this chapter the results of an e.p.r. examination of $Fe_2(SR)_2(NO)_4$ in various polar solvents are reported.

In chapter 2 the results of attempts to carry out alkanethiolate exchange reactions with $Fe_2(SR)_2(CO)_6$ to produce suitably functionalised R groups prior to conversion to their nitrosyl analogues were reported. In this chapter the results of attempts to carry out similar exchange reactions on $Fe_2(SR)_2(NO)_4$ are reported.

4.2 Experimental.

4.2.1 Materials and Instruments.

Samples of $Fe_2(SR)_2(NO)_4$ was prepared as described in chapter 2 from $Fe_2(SR)_2(CO)_6$, and by literature methods from $Fe_2I_2(NO)_4$[14]. All manipulations were carried out under an atmosphere of dry nitrogen: all organic solvents were purified, dried, and purged with dry nitrogen before use. All chemicals employed were Analar grade or the purest available.

E.p.r. spectra were measured, usually at 240K, in 1mm quartz capillaries using a Bruker 200D Spectrometer. Di-t-butyl nitroxide was employed as the standard for the measurement of line positions. N.m.r. spectra were measured at ambient spectrometer temperature (308K) using a Bruker WP-80 Spectrometer.

4.2.2 Exchange Reactions.

(a) Samples (0.10g) of $Fe_2(SEt)_2(NO)_4$ were dissolved in 50 ml portions of DMF, THF, EtOH or toluene and Pr^iSH (1 ml) was then added, and the mixture stirred under nitrogen, at room temperature, for 72 hours. The solvent and volatile products were then removed on the vacuum system, and the residual solid was examined by ^1H n.m.r. spectroscopy in $CDCl_3$.

(b) Samples (0.10g) of $Fe_2(SR)_2(NO)_4$ were dissolved in 50 ml portions

of THF and R'SH (1 ml) was then added. The mixtures were stirred under nitrogen, at room temperature, for 72 hours and then worked up and examined as above. The exchange reaction with H_2S was carried out in a sealed 5 dm^3 vessel at 1 atm. pressure. The acid $Fe_2(SH)_2(NO)_4$ was characterised by comparison with data reported by Beck[15].

4.2.3 Attempts to isolate $[Fe(NO)_2(SR)_2]^-(PPN)^+$.

(a) To $Fe_2(SMe)_2(NO)_4$(0.25g) in dry deoxygenated DMF (20 ml) was added MeSNa (1.00g). This mixture was stirred for 1 hour under nitrogen. The resulting solution was transferred to a 150cm x 2.5 cm silica gel dry column and eluted with DMF. The compound ran as a dark green band followed by brown streaks. Examination of the sections of the column revealed that the green band contained a mixture of $[Fe(NO)_2(DMF)_2]^+$, $Fe(NO)_2(SMe)(DMF)$ and $[Fe(NO)_2(SMe)_2]^-$, identified by e.p.r. spectroscopy. Extracts of the brown streaks were diamagnetic, and n.m.r. examination revealed the presence of $Fe_2(SMe)_2(NO)_4$.

(b) Attempts to isolate $[Fe(NO)_2(SR)_2]^-(PPN)^+$ by the addition of stoichiometric quantities of $[PPN]^+Cl^-$ and RSNa to THF, Et_2NH and DMF solutions of $Fe_2(SR)_2(NO)_4$ resulted in the production of mixtures of $[Fe(NO)_2(SR)_2]PPN$ and $Fe_2(SR)_2(NO)_4$. All attempts to isolate $[Fe(NO)_2(SR)_2]PPN$ by chromatography or fractional recrystalisation resulted in the conversion of $[Fe(NO)_2(SR)_2]PPN$ into $Fe_2(SR)_2(NO)_4$.

4.3 Results and Discussion.

4.3.1 Bridging ligand exchange reactions

In chapter 2, the results of a series of bridging ligand exchange reactions were recorded for a range of esters $Fe_2(SR)_2(CO)_6$. These reactions were performed in an attempt to produce suitably functionalised compounds prior to conversion to their nitrosyl analogues. In this section the results of a study of the bridging ligand exchange reactions of the esters of $Fe_2(SR)_2(NO)_4$ are reported.

$Fe_2(SEt)_2(NO)_4$ was reacted with an excess of Pr^iSH in a range of solvents (table 4.1).

Table 4.1: Solvent dependence of the reaction between $Fe_2(SEt)_2(NO)_4$ and Pr^iSH.

Solvent	Product Composition (%)	
	$Fe_2(SPr^i)_2(NO)_4$	$Fe_2(SEt)_2(NO)_4$
DMF	100	0
THF	100	0
EtOH	86	14
Toluene	62	38
Cyclohexane	60	40

In all solvents examined exchange was observed. However, the extent

of this exchange was dependent upon the polarity of the solvent. In the polar solvents, DMF and THF, complete ligand exchange was observed, whilst in non-polar solvents such as benzene, ligand exchange was not complete. To test the generality of this exchange reaction a range of esters of $Fe_2(SR)_2(NO)_4$ were allowed to react with an excess of thiol in THF. These mixtures were evaporated to solid after 72 hours and the composition of the reaction products determined by ^1H n.m.r. spectroscopy. The spectra obtained showed the exchange reaction to be general and to be complete or almost so (table 4.2).

Table 4.2: Results of exchange reactions of $Fe_2(SR)_2(NO)_4$ with added thiols R'SH in THF.

R	R'	Product Composition (%)	
		$Fe_2(SR')_2(NO)_4$	$Fe_2(SR)_2(NO)_4$
CH_3	H	90	10
CH_3	n-C_3H_7	100	0
C_2H_5	i-C_3H_7	100	0
i-C_3H_7	CH_2COOH	95	5
t-C_4H_9	i-C_3H_7	60	40

In all of these reactions the total material recovered was greater than 95%. The spectra obtained demonstrated the reactions to be clean with negligible decomposition; no products of any side reactions were observed.

In an attempt to examine the alkanethiol exchange process in toluene-d_8 by ^{1}H n.m.r. a sample of $Fe_2(SMe)_2(NO)_4$ was reacted with a 10:1 excess of $PhCH_2SH$. Examination of this mixture at intervals revealed a very slow rate of exchange, the reaction having not reached equilibrium after one year. Throughout this examination no decomposition was observed in the tube and no extraneous peaks appeared in the ^{1}H n.m.r. spectra. The alkyl exchange reaction must proceed via a mixed ester intermediate of $Fe_2(SR)(SR')(NO)_4$. The ^{1}H n.m.r. spectra of the samples from the solvent and the THF study were recorded in $CDCl_3$; in no case was resolution achieved of peaks unequivocally assignable to the mixed ester products. However, in the exchange examination in toluene-d_8, peaks assignable to the mixed product were resolved with identical chemical shift to that of either of the esters, $Fe_2(SMe)_2(NO)_4$ and $Fe_2(SCH_2Ph)_2(NO)_4$, but with different $\Delta\nu$ values; in the case of the methyl analogue this was smaller *ca.* 2.0 Hz against 5.8 Hz, and in the case of the methylene protons in the benzyl analogue, larger, *ca.* 6.0 Hz against 2.7 Hz.

These alkanethiol exchange reactions are of synthetic value and are superior to those described in chapter 2, which were based upon exchange reactions of $Fe_2(SR)_2(CO)_6$ prior to its conversion to its nitrosyl analogue. Although a bridging ligand exchange process does occur, it was not of general utility and was not always a clean reaction. Rauchfuss and Weatherill[14] developed a synthetically useful reaction for the preparation of $Fe_2(SR)_2(NO)_4$ from $Fe_2I_2(NO)_4$ by the reaction of stoichiometric quantities of $Fe_2I_2(NO)_4$ with the appropriate thiol and base. This is a good synthetic route; however,

for the preparation of esters with functionalised R groups, in particular those containing substrates which render the ester water soluble, this alkanethiol exchange reaction with preformed $Fe_2(SR)_2(NO)_4$ is better.

4.3.2 E.p.r. examinations of $Fe_2(SR)_2(NO)_4$

In chapter 3, the results of an n.m.r. examination of $Fe_2(SR)_2(NO)_4$ in various solvents was discussed. The fact that well resolved spectra are obtained in the majority of solvents examined is due to the continued existence of the dimer in solution. The robustness of the iron-sulphur ring is illustrated by refluxing an equimolar mixture of $Fe_2(SMe)_2(NO)_4$ and $Fe_2(SEt)_2(NO)_4$ in chloroform under nitrogen for four hours, where negligible decomposition or production of the mixed ester $Fe_2(SMe)(SEt)(NO)_4$ is observed. However, if this is repeated in DMF, then the mixed ester, identifiable by mass spectroscopy, is readily generated. In the n.m.r. examination of MERR in DMF-d_7, well resolved spectra were observed to broaden and collapse with time; this was coupled with a shift in resonance to low field, due to the generation of paramagnetic mono-iron species in solution.

The esters $Fe_2(SR)_2(NO)_4$ (R=Me,Et,Pr^i,Bu^t and $PhCH_2$) all gave weak e.p.r. absorptions when dissolved in DMF: the spectra were centred at g=2.03 and were broad with no resolved hyperfine coupling. Addition of thiols enhanced the spectral intensity, although solutions of $Fe_2(SR)_2(NO)_4$ in RSH alone were e.p.r. silent. Upon subsequent

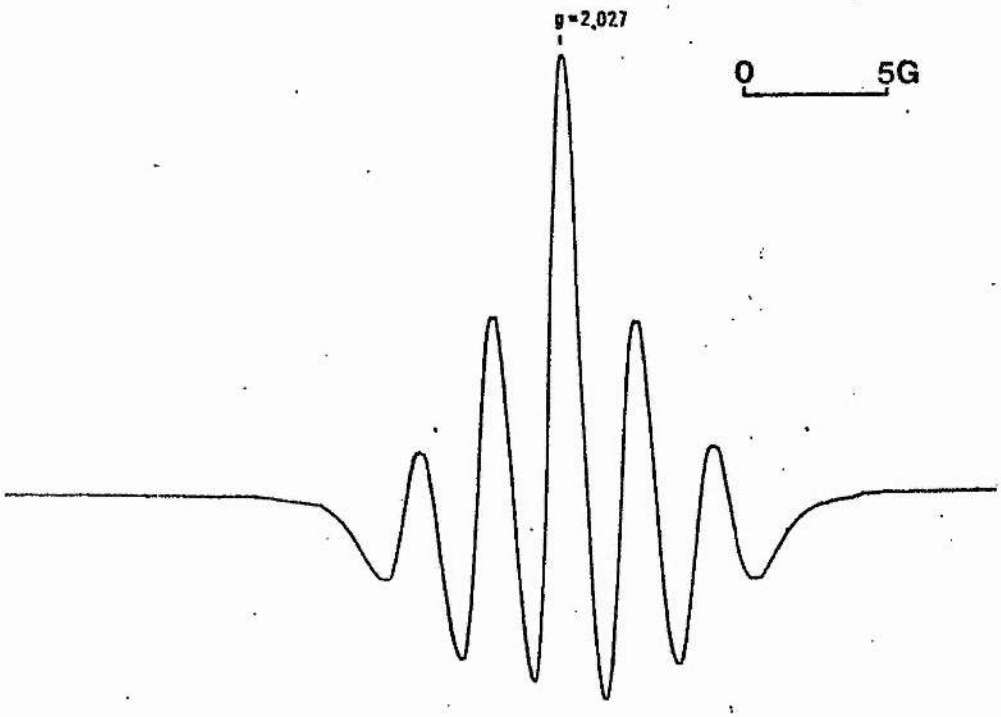


Fig. 4.1; E.p.r. spectrum of $[Fe(NO)_2(SBu^t)_2]^-$

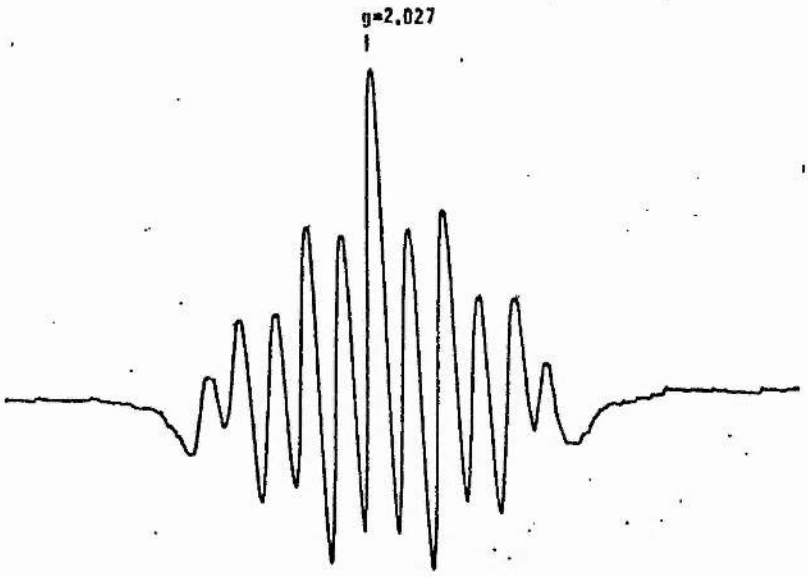


Fig. 4.2; E.p.r. spectrum of $[Fe(NO)_2(SPr^i)_2]^-$

addition of a trace of MeS^-, which acts as a base, a major enhancement in spectral intensity and resolution occurred. All of the species generated were isotropic and demonstrated resolved hyperfine coupling, caused by magnetic coupling between the iron atom's unpaired electron and nearby magnetic nuclei in the complex. As in n.m.r. spectroscopy, there are 2nI+1 energy levels. So for an e.p.r. spectrum of a paramagnetic species containing two coupled ^{14}N nuclei (I=1), there are five components labelled M_I=+2,+1,0,-1,-2 with relative intensities 1:2:3:2:1.

By the use of various alkanethiolates, it was possible to identify the generated paramagnetic species. Addition of an excess of Bu^tS^- to any ester $Fe_2(SR)_2(NO)_4$, resulted in the generation of spectra which were independent of the alkyl groups of the ester (fig. 4.1). The spectra obtained were composed solely of a quintet of relative intensity 1:2:3:2:1, assigned to the coupling of the two ^{14}N nuclei;I=1 of the two nitrosyl ligands. Repeating this experiment, substituting Pr^iS^- for Bu^tS^- resulted in the generation of spectra containing a quintet. However, in addition, each of the five peaks were split into a triplet with binomial intensity 1:2:1 (fig. 4.2), due to the coupling of two nuclei with I=1/2. Pr^iS^- possesses a single proton directly bonded to the C-S carbon, and coordination of two thiolato ligands to the $[Fe(NO)_2]^+$ fragment to form $[Fe(NO)_2L_2]^-$ would result in the coupling of two protons (I=1/2). Bu^tS^- has no protons attached to its C-S carbon and hence this coupling will, as was found, be absent. If this assignment of the composition of the paramagnetic species is correct, then substitution of RCH_2S^- for Pr^iS^- should result in each peak in the nitrogen's quintet being split into

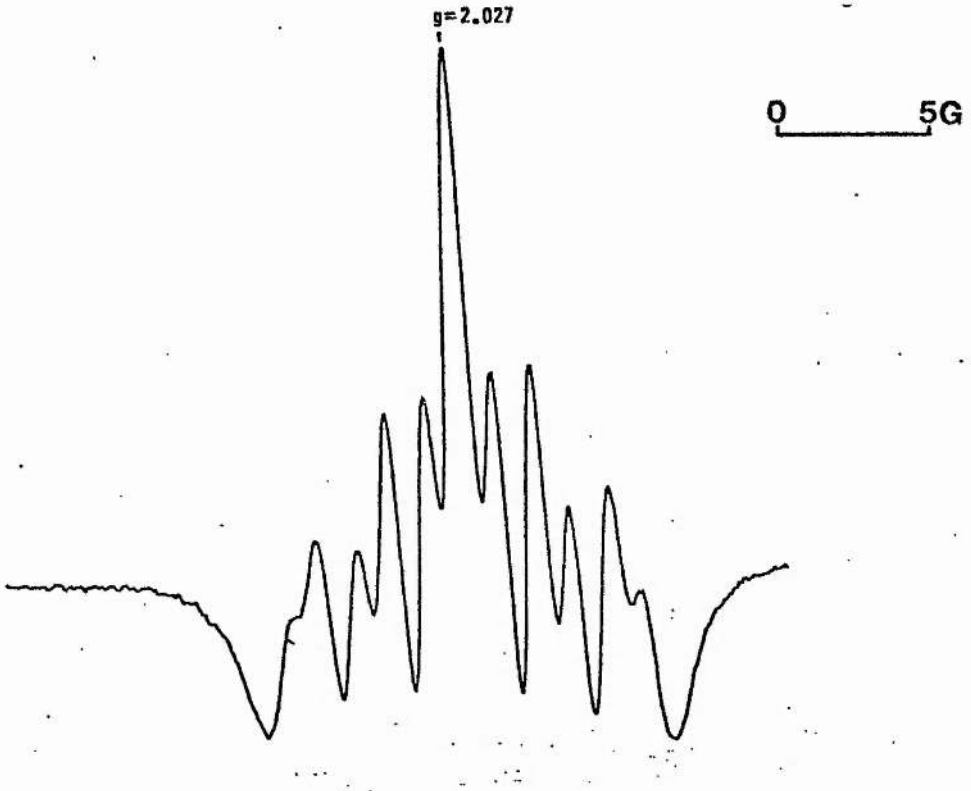


Fig. 4.3; E.p.r. spectrum of $[Fe(NO)_2(SCH_2Ph)_2]^-$

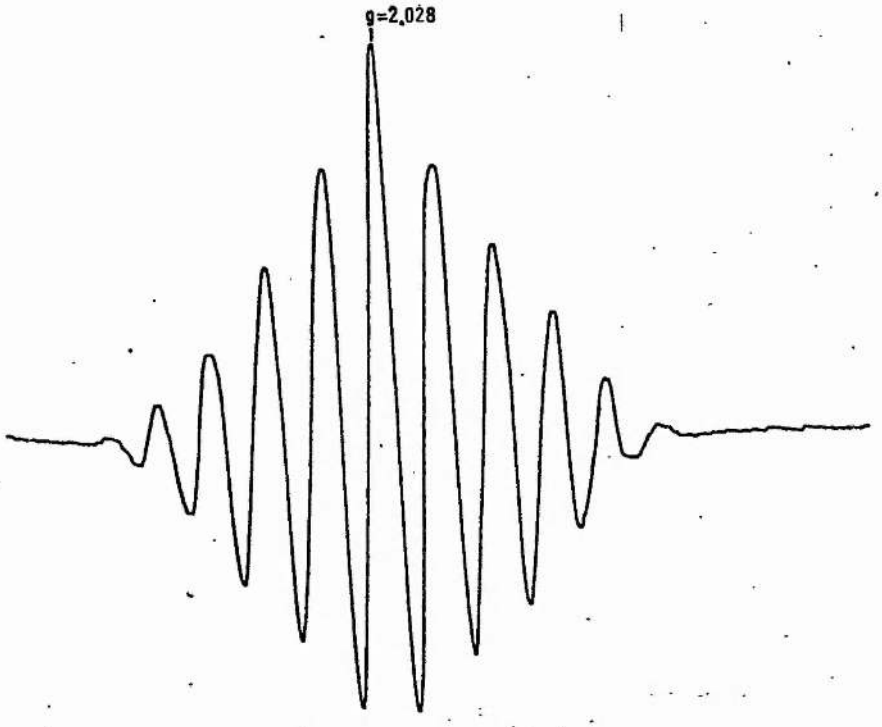


Fig. 4.4; E.p.r. spectrum of $[Fe(NO)_2(SMe)_2]^-$

a quintet of relative intensities 1:4:6:4:1. Likewise, addition of MeS^- would result in each peak being split into a heptet (1:6:15:20:15:6:1). On performing the appropriate substitution, the intensities were observed as anticipated (fig. 4.3 and 4.4), thus confirming the composition as being that proposed by McDonald[1] for similar species. The generation of these paramagnetic species from $Fe_2(SR)_2(NO)_4$ may therefore be summarised:

$$Fe_2(SR)_2(NO)_4 + 2RSH \xrightarrow{base} 2[Fe(SR)_2(NO)_2]^-$$

Table 4.3: E.p.r. data for $[Fe(NO)_2(SR)_2]^-$ complexes.

R	g	A(^{14}N)/G	A(^{1}H)/G
H	2.028	2.7	0.5 (2H)
Me	2.028	2.1	2.1 (6H)
Et	2.027	2.6	2.0 (4H)
i-Pr	2.027	2.5	1.3 (2H)
t-Bu	2.027	2.7	- (0H)
$PhCH_2$	2.027	2.4	1.4 (4H)

In addition to the generation of these e.p.r. spectra by the addition of RS^- to DMF solutions of $Fe_2(SR)_2(NO)_4$, spectra could be generated by the addition of NaSH. It was found that the e.p.r. spectra thus produced were acid/base dependent, acidification resulting in the reversible conversion of $[Fe(NO)_2(SH)_2]^-$ into $Fe(NO)_2(SH)(SH_2)$: g=2.031; A(N) 2.00G; A(H) 1.90G. Attempts to add a second proton to the complex to form $[Fe(NO)_2(SH_2)_2]^+$, even by the bubbling of H_2S through the solution, were unsuccessful.

$$[Fe(NO)_2(SH)_2]^- \rightleftharpoons Fe(NO)_2(SH)(SH)_2 \not\rightleftharpoons [Fe(NO)_2(SH_2)_2]^+$$

McDonald[1] reported that the observed signal intensities of the paramagnetic complexes generated by the action of nitric oxide on solutions of iron(II) salts were dependent upon the pH of the mixtures. The greater the pH, the stronger the observed spectrum. This he suggested was due to the existence of a mononuclear/dinuclear equilibrium:

$$2[Fe(NO)_2L_2]^- \rightleftharpoons Fe_2L_2(NO)_4 + 2L^-$$

However, no report was found in the chemical literature of attempts to isolate any of these dinuclear complexes generated in this manner. In attempts to isolate analytically pure samples of the mono-anion $[Fe(NO)_2(SR)_2]^-$, as either its sodium or PPN^+ salt, proved unsuccessful (cf. experimental). In all attempts the extracted mixture was found to contain the dinuclear $Fe_2(SR)_2(NO)_4$ and indeed attempts to separate the two resulted in the conversion of the mono-iron complex into $Fe_2(SR)_2(NO)_4$. These attempts thus demonstrate the reversibilty of the mononuclear/dinuclear equilibrium. The pH dependency of the equilibrium in DMF is illustrated by the difference in action of RSH and of RS^- on $Fe_2(SR)_2(NO)_4$. Addition of the acidic RSH resulted in little spectral enhancement, whilst addition of the base RS^-, resulted in the production of strong e.p.r. spectra due to $[Fe(NO)_2(SR)_2]^-$. Subsequent, acidification of solutions containing $[Fe(NO)_2(SR)_2]^-$ resulted in a loss of spectral intensity.

In addition to g-centres ca. 2.03, the $[Fe(NO)_2(SR)_2]^-$ complexes were found to possess hyperfine couplings to nitrogen and hydrogen similar to those previously observed for species generated from iron(II) salts[1-6]. The magnitude of the hyperfine coupling is proportional to the degree of interaction between the unpaired electron and orbitals of adjacent atoms with nuclei with $I \neq 0$. Comparison of the values obtained for $[Fe(NO)_2(SR)_2]^-$ (table 4.3) reveals that, as the protons are replaced on the α-carbon atom by alkyl substituents, there is an increase in the magnitude of the nitrogen hyperfine coupling resulting from a stronger interaction with the nitrosyl's orbitals. On changing from R=Me to Bu^t there is a resultant increase in coupling to nitrogen of some 29%.

It is more difficult to comment on the degree of interaction with the alkanethiolato groups since it was not possible to resolve any coupling to ^{13}C. However, on changing from R=Me to Pr^i there is a decrease of 38% in the coupling to the α-protons. This suggests that there may be a reduction in the interaction between the unpaired electron and the alkanethiolato groups on replacement of protons on the α-carbon.

4.3.3 Solvent studies of $Fe_2(SR)_2(NO)_4$.

In the examination of $Fe_2(SR)_2(NO)_4$ in DMF-d_7 by n.m.r. spectroscopy, it was found that, as the solution aged, the peaks broadened and collapsed. The rate of this process was temperature dependent. When a solution of either $Fe_2(SMe)_2(NO)_4$ or $Fe_2(SPr^i)_2(NO)_4$ in DMF was heated to 350K for 5 minutes, and subsequently cooled to 240K, the spectral intensity was much enhanced

over that of the initial solution and, in the case of R=Pr^i at least, it was clear that two paramagnetic complexes were present in approximately equimolar concentrations. Comparison of the spectra obtained from $Fe_2(SPr^i)_2(NO)_4$ in DMF, DMF-d_7 and dimethylacetamide (DMA) showed that these two species were $[Fe(NO)_2(Solv)_2]^+$ and $Fe(NO)_2(SR)(Solv)$ in which there is hyperfine coupling to the unique proton in DMF in addition to those involving the ^{14}N nuclei of the two nitrosyl groups and the α-protons of the SR group (table 4.4).

Table 4.4: E.p.r. data for Solvo complexes of $Fe_2(SR)_2(NO)_4$ with DMF, DMF-d_7 and DMA.

Complex	g	$A(^{14}N)$/G	$A(^1H)(SR)$/G	A(X)/G
(1) Solvo-complexes from $Fe_2(SPr^i)_2(NO)_4$				
$[Fe(NO)_2(DMF)_2]^+$	2.033	2.4 (2N)	-	4.0 (2H)
$Fe(NO)_2(SPr^i)(DMF)$	2.027	2.6 (2N)	1.3 (1H)	4.6 (1H)
$[Fe(NO)_2(DMF\text{-}d_7)_2]^+$	2.033	2.5 (2N)	-	-
$Fe(NO)_2(SPr^i)(DMF\text{-}d_7)$	2.027	2.5 (2N)	1.3 (1H)	-
$[Fe(NO)_2(DMA)_2]^+$	2.033	2.5 (2N)	-	-
$Fe(NO)_2(SPr^i)(DMA)$	2.027	2.5 (2N)	1.3 (1H)	-
(2) Solvo-complexes from $Fe_2(SMe)_2(NO)_4$				
$[Fe(NO)_2(DMF)_2]^+$	2.033	2.4 (2N)	-	4.0 (2H)
$Fe(NO)_2(SMe)(DMF)$	2.027	2.4 (2N)	4.5 (3H)	4.6 (1H)

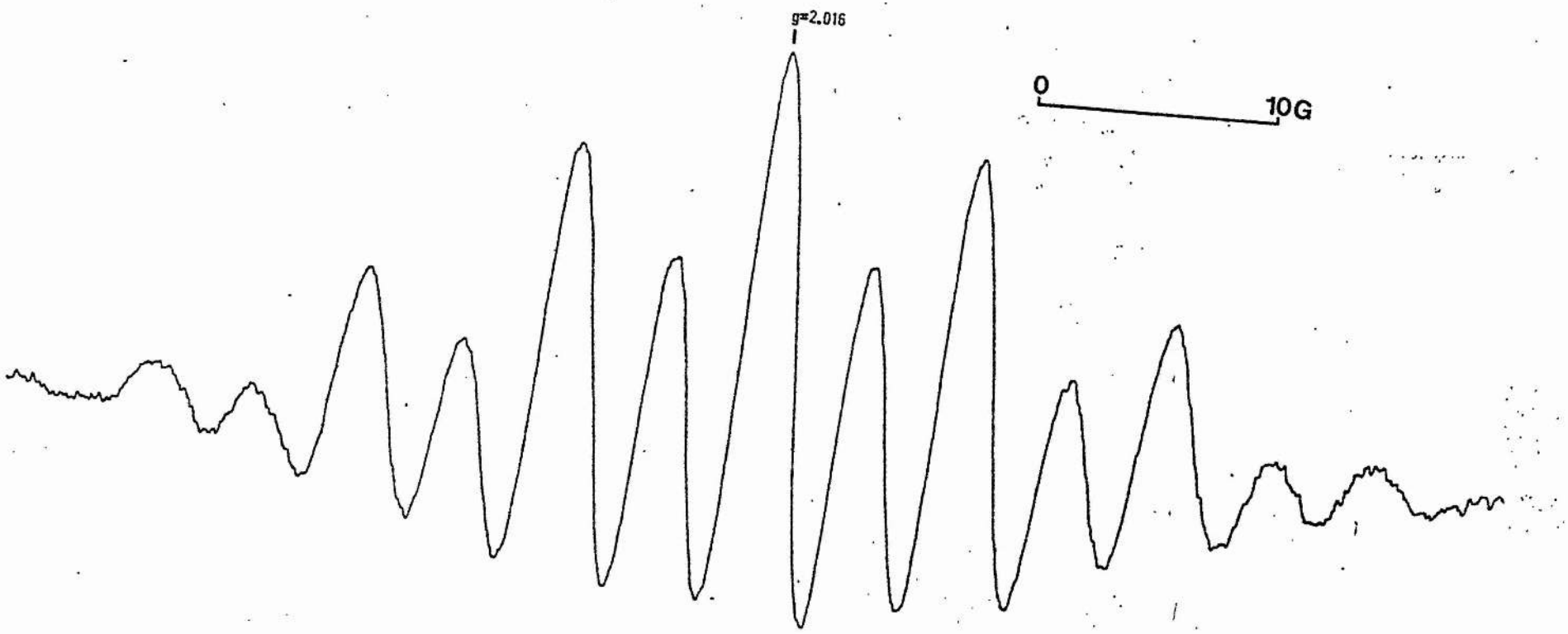


Fig. 4.5; E.p.r. spectrum of $[Fe(NO)_2(pyridine)_2]^+$

The absence of any nitrogen coupling other than that to the two nitrosyl ligands, and the presence of coupling to the unique proton of DMF, implies that the solvent coordinates via its carbonyl group. DMF-d_7 contains one unique deuterium atom (I=1) and coordination of two molecules of solvent via their carbonyl groups yields five components in the e.p.r. spectrum with relative intensities 1:2:3:2:1. However, inspection of the DMF-d_7 spectrum revealed no identifiable deuterium coupling. Magnitudes of experimentally observed hyperfine couplings are proportional to A_o and itself is proportional to the ratio of the (magnetic moment)/(nuclear spin) of the nuclei. The ratio of A_o for ^1H to ^2H is 6.5:1[16]. from the experimentally observed coupling constant for the unique proton in DMF a value of 0.6G for A(^2H) may be deduced for the deuterium hyperfine coupling. This reduction results in the deuterium hyperfine coupling not being resolved.

In solutions of $Fe_2(SR)_2(NO)_4$ in DMF, DMF-d_7 and DMA complexes of type $[Fe(NO)_2(Solv)_2]^+$ were formed (fig. 4.5). Similar di-solvated complexes were formed in a range of hetero-aromatic solvents(table 4.5),

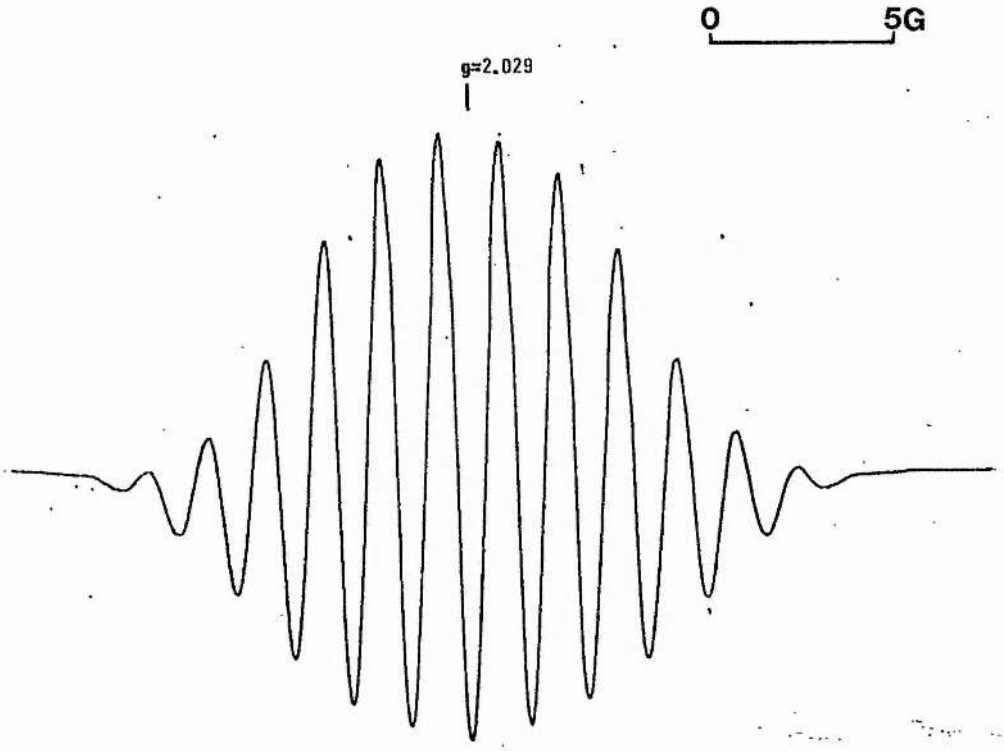


Fig. 4.6; E.p.r. spectrum of $Fe(NO)_2(SMe)(NHEt_2)$

Table 4.5: E.p.r. data for $[Fe(NO)_2(Solv)_2]^+$ complexes.

Solvent	g	$A(^{14}N)/G$	$A(X)/G^c$
DMF	2.033	2.4 (2N)	4.0 (2H)
DMF-d_7	2.033	2.5 (2N)	a
DMA	2.033	2.5 (2N)	a
Pyridine	2.016	4.5 (2N)	8.9 (2N)
2,6-Dimethylpyridine	2.031	2.3 (2N)	4.6 (2N)
2,4,6-Trimethylpyridine	2.030	b	b
Quinoline	2.032	2.2 (2N)	4.4 (2N)

a/ No resolution of hyperfine coupling to hydrogen or nitrogen in coordinated solvent molecules.

b/ No resolution of any hyperfine couplings; identity of paramagnetic complex doubtful. c/ X represents ^1H or ^{14}N in coordinated solvent molecules.

whilst complexes of type $Fe(NO)_2(SR)(Solvent)$, which were also formed in DMF, DMF-d_7 and DMA, appeared to be formed in a number of non aromatic solvents (table 4.6, fig. 4.6).

Table 4.6: E.p.r. data for $Fe(NO)_2(SR)(Solv)$ complexes.

Solvent	R	g	$A(^{14}N)/G$	$A(^1H)(SR)/G$	A(X)/G
DMF	Pr^i	2.027	2.6 (2N)	1.3 (1H)	4.6 (1H)
DMF-d_7	Pr^i	2.027	2.6 (2N)	1.3 (1H)	a
DMA	Pr^i	2.027	2.5 (2N)	1.3 (1H)	a

DMF	Me	2.027	2.4 (2N)	4.5 (3H)	4.6 (1H)
DMSO	Me	2.032	6.0 (2N)	3.2 (3H)	a
NH_3	Me	2.029	b	b	b
Et_2NH	Me	2.029	4.0 (2N)	2.0 (3H)	a
Pyrrolidine	Me	2.029	3.9 (2N)	2.0 (3H)	a
Piperidine	Me	2.029	4.2 (2N)	2.1 (3H)	a
Piperidine	CH_2Ph	2.029	4.2 (2N)	2.0 (2H)	a
H_2O	CH_2COOH	2.030	b	b	b

In none of the latter class, except for DMF, was any hyperfine coupling observed to either hydrogens or nitrogens of coordinated solvent molecules. This is presumably due to fast solvent exchange. However, in all cases, attempts to reduce the rate of solvent exchange by reducing the sample temperature in increments to the freezing temperature of the solvent proved unsuccessful in resolving this coupling. Similar species[17] have been previously assigned to $Fe(NO)_2X(Solv)$, and by analogy with the DMF solvo-complexes $Fe(NO)_2(SR)(DMF)$, these species may be assigned constitutions of the same type. In liquid ammonia solution at 200K, $Fe_2(SMe)_2(NO)_4$ yielded a weak e.p.r. spectrum having g=2.029, in which no hyperfine coupling were resolvable: by analogy with the aliphatic amines this species may be $Fe(NO)_2(SMe)(NH_3)$.

Examination, by e.p.r. spectroscopy at 275K, of an aqueous solution of $Fe_2(SCH_2COOH)_2(NO)_4$ revealed a weak unresolved absorption, centred at g=2.030. In water/ethanol mixtures, the complex $[Fe(NO)_2(H_2O)_2]^+$ is reported[2] to give a broad unresolved absorption at g=2.033. The di-deprotonated analogue[2], $[Fe(NO)_2(OH)_2]^-$, at g=2.027

demonstrates resolvable coupling to ^{14}N. By analogy with these results and those obtained above for $Fe_2(SR)_2(NO)_4$ in a range of non-aromatic solvents the species with g=2.030 could either be $Fe(NO)_2(SCH_2COOH)(OH_x)$, where x=1 or 2 or the mono-deprotonated aquo species $Fe(NO)_2(OH)(OH_2)$.

With the exception of the solvo-complexes formed in DMF and DMA, all of the other solvo-complexes were formed at room temperature or below. This formation is significant in that it demonstrates the diamagnetic esters $Fe_2(SR)_2(NO)_4$ can spontaneously and very readily form paramagnetic species, simply upon dissolution in a polar coordinating medium, typical of physiological environments[7-10,18,19]; this is discussed in chapter 7.

Despite any residual uncertainty about the constitution of the solvo-complexes of $Fe_2(SR)_2(NO)_4$ formed in DMA, DMSO and aliphatic amines, it is clear that there are two major points of difference between the solvo-complexes formed by hetero-aromatic amines and by aliphatic amines. The hetero-aromatic amines displace all of the coordinated RS groups and the resulting complexes show resolved hyperfine coupling to the coordinated solvent. In contrast, the aliphatic amines permit the coordination of one RS group to $[Fe(NO)_2]^+$ and the resulting complexes show no coupling to the solvent.

For a possible rationalisation of the differences observed in the coordination of mono-iron fragments to aliphatic and hetero-aromatic amines the metal-ligand binding requires consideration. Although no formation constants appear to be available for the interaction of

amines acting as both solvent and as ligand towards a d^9 metal ion, the properties of the amines themselves can be considered and compared. The spectrochemical f values for ammonia, the aliphatic amines and heteroaromatic amines are[20] very similar and allow little distinction between the classes of ligand. However, the use of a two-dimensional spectrochemical series[21] shows that whereas the aliphatic amines are essentially involved only in σ-bonding with central metal atoms, hetero-aromatic in addition to their σ-donor properties are also strong π acceptors. This difference will be accentuated by an electron rich π system, and consequently the metal-ligand π back bonding can be suggested as the source of the differences between the two classes of ligand. The more powerful metal-ligand interaction between $[Fe(NO)_2]^+$ and hetero-aromatic amines resulting in the displacement of all of the alkanethiolate ligands. The strong interaction between $[Fe(NO)_2]^+$ and the hetero-aromatic solvents is observed, particularly in the case of pyridine, by the magnitude of the hyperfine coupling to the nitrogen in the solvent molecules.

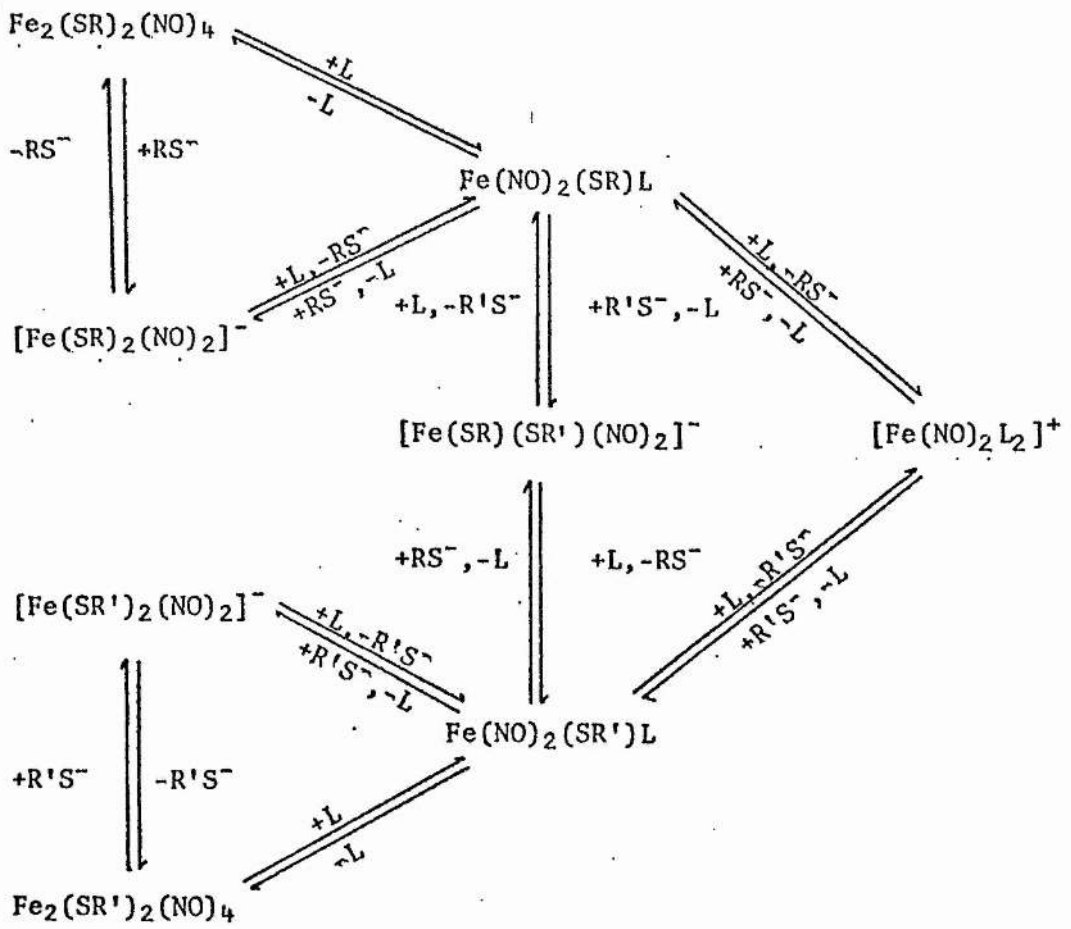
4.3.4 Alkanethiolato ligand exchange processes in iron-nitrosyls

In the recording of the spectra of $[Fe(NO)_2(SR)_2]^-$, there was no significant variation in the intensity of the observed spectra with time indicating that the equilibrium:

$$Fe_2(SR)_2(NO)_4 + 2RS^- \rightleftharpoons 2[Fe(NO)_2(SR)_2]^-$$

is obtained relatively quickly. This is unlike in the solvolysis of $Fe_2(SR)_2(NO)_4$ in DMF where it was found that the intensity of the observed spectra was time dependent. Although the concentration of $[Fe(NO)_2(SR)_2]^-$ appeared independent of time, it was dependent upon temperature, the magnitude of the observed spectra being significantly increased at lower temperatures.

The foregoing series of observations, namely (i) that the rate of alkanethiol exchange is faster in more polar, coordinating, solvents; (ii) that in these solvents the esters $Fe_2(SR)_2(NO)_4$ readily yield mono-nuclear solvo-complexes; and (iii) that exchange of RS groups occurs readily in the mononuclear complexes $[Fe(SR)_2(NO)_2]^-$; allow the formulation of a tentative mechanism for the exchange reaction.



This scheme contains all the potentially important equilibria involved in the conversion of $Fe_2(SR)_2(NO)_4$ to $Fe_2(SR')_2(NO)_4$, and with the exception of $[Fe(NO)_2(SR)(SR')]^-$, all of the complexes in the scheme and all of the individual equilibria have been observed for at least one combination R,R'. In solvents such as pyridine, the exchange appears to proceed solely via $[Fe(NO)_2L_2]^+$; in solvents such as Et_2NH, solely via $Fe(NO)_2(SR)L$; and in solvents such as DMF, via both routes.

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CHAPTER FIVE

SOLUTION PHASE E.P.R. STUDY OF $Fe_2I_2(NO)_4$ AND ITS REACTIONS WITH VARIOUS ANIONIC LIGANDS.

5.1 Introduction.

Rauchfuss and Weatherill[1] demonstrated that the μ_2-iodo complex $Fe_2I_2(NO)_4$ in THF reacts with thiols, in the presence of triethylamine, in a synthetically useful route to the μ_2-thiolato complex $Fe_2(SR)_2(NO)_4$.

$$Fe_2I_2(NO)_4 + 2RSH + 2Et_3N \longrightarrow Fe_2(SR)_2(NO)_4 + Et_3NH^+I^-$$

$Fe_2I_2(NO)_4$ is a useful catalyst for alkene polymerisation[2-4], in connection with which it and its reactions have been extensively examined[5-7]. The results of conductance measurements of dilute solutions of $Fe_2I_2(NO)_4$ in DMF have been previously reported by Piazza and Innorta[8]. The molar conductivity thus obtained were claimed to demonstrate that the complex was completely dissociated;

$$Fe_2I_2(NO)_4 \longrightarrow 2[Fe(NO)_2]^+ + 2I^-$$

and that the resultant $[Fe(NO)_2]^+$ ion is essentially unsolvated. In chapter 4, the results are reported of an e.p.r. study of the dissociation of $Fe_2(SR)_2(NO)_4$ in DMF is reported in which the

mono-iron species $Fe(NO)_2(SR)(Solv)$ and $[Fe(NO)_2(Solv)_2]^+$ are characterised. In this chapter a similar study of $Fe_2I_2(NO)_4$ and its reactions with thiols, halides, and pseudohalides are reported, and compared with species produced from iron(II) salts, nitric oxide and various anionic ligands[9-12]. The solvent dependence of some of these reactions is also reported as well as the result of a study of the conversion of $Fe_2I_2(NO)_4$ into $Fe_2(SR)_2(NO)_4$.

5.2 Experimental.

5.2.1 Materials and Instruments.

Literature methods[13-15] were employed for the preparation and purification of $Fe_2Br_2(NO)_4$, $Fe_2I_2(NO)_4$ and $Fe_2(SR)_2(NO)_4$. Solutions for e.p.r. examinations were prepared using dry, redistilled solvents, deoxygenated with a stirring nitrogen stream; all manipulations of solutions were made under dry nitrogen. All chemicals employed were Analar grade or the purest available and were dried before use.

E.p.r. spectra were measured in 1 mm quartz capillaries using a Bruker ER 200D Spectrometer. Di-t-butyl nitroxide was employed as the standard in the determination of line positions; diphenyl picryl hydrazyl was used as the standard in the determination of the concentration of paramagnetic species.

5.3 Results and Discussion.

5.3.1 Examination of $Fe_2I_2(NO)_4$ in DMF.

In chapter 4 the results of an examination of the dissociation of $Fe_2(SR)_2(NO)_4$ in various solvents, but in particular DMF, are reported. The concentration of paramagnetic mono-iron species thus generated in DMF were low. Repeating this study, but substituting the μ_2-iodo complex $Fe_2I_2(NO)_4$ for the solute, produced solutions which exhibited strong e.p.r. signals. Examination of dilute solutions (2×10^{-4} M) of $Fe_2I_2(NO)_4$ in DMF yielded spectra assignable to a single (detectable) species, a quintet with g-centre ca. 2.032 due to $[Fe(^{14}NO)_2]^+$. No detectable hyperfine coupling to either ^{127}I (I = 5/2) or the hydrogens of coordinated solvent molecules were observed even at low temperatures. This observation is consistent with conductance measurements at this concentration[8], which suggested complete ionisation of the $Fe_2I_2(NO)_4$.

$$Fe_2I_2(NO)_4 \longrightarrow 2[Fe(NO)_2]^+ + 2I^-$$

In addition Piazza and Innorta[8] deduced, by application of Walden's rule in the form $\Lambda_i \times r_i$ = constant for a medium of fixed viscosity, that the cation $[Fe(NO)_2]^+$ is unsolvated in the concentration range 5×10^{-5} to 10^{-3} M.

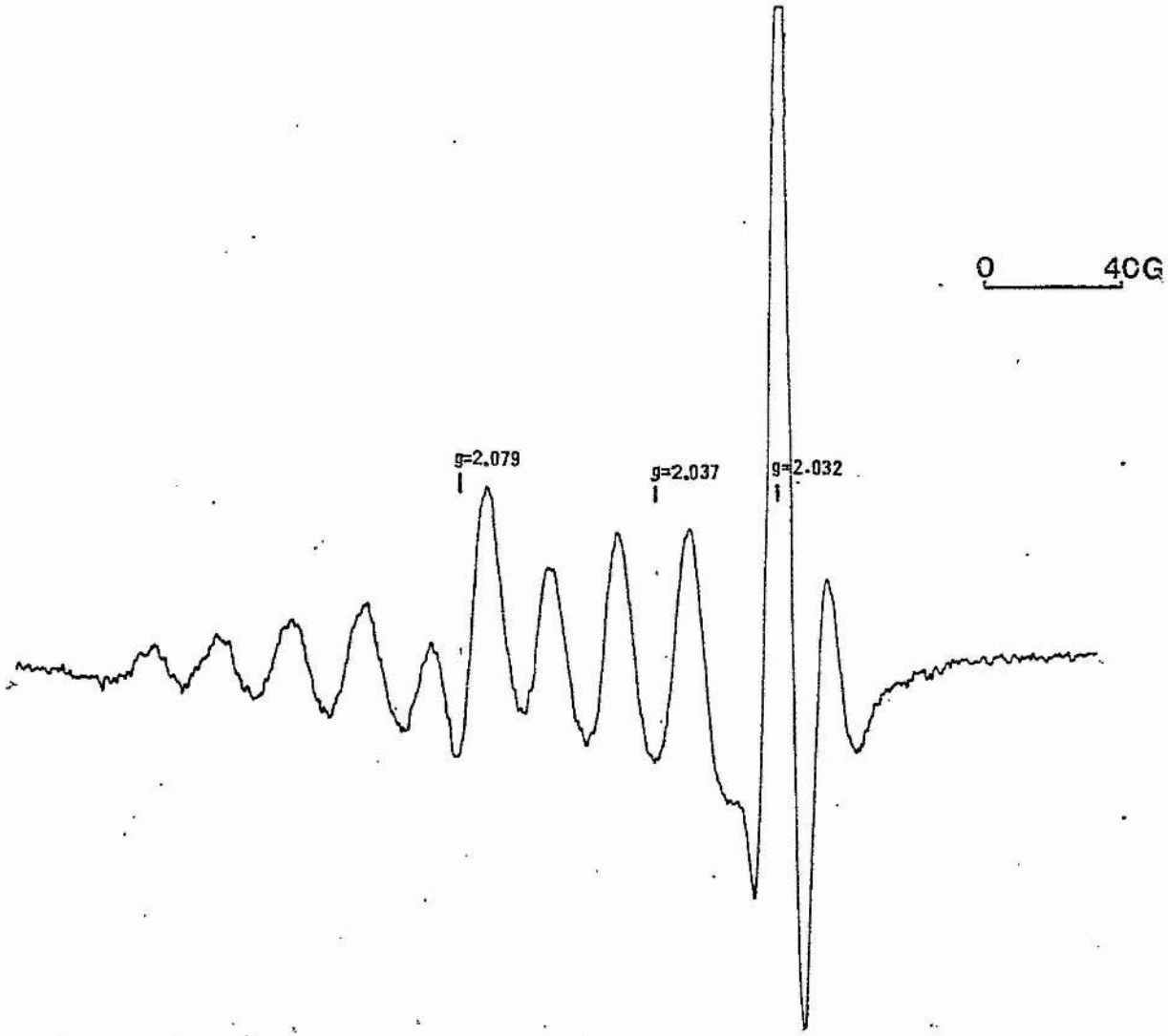
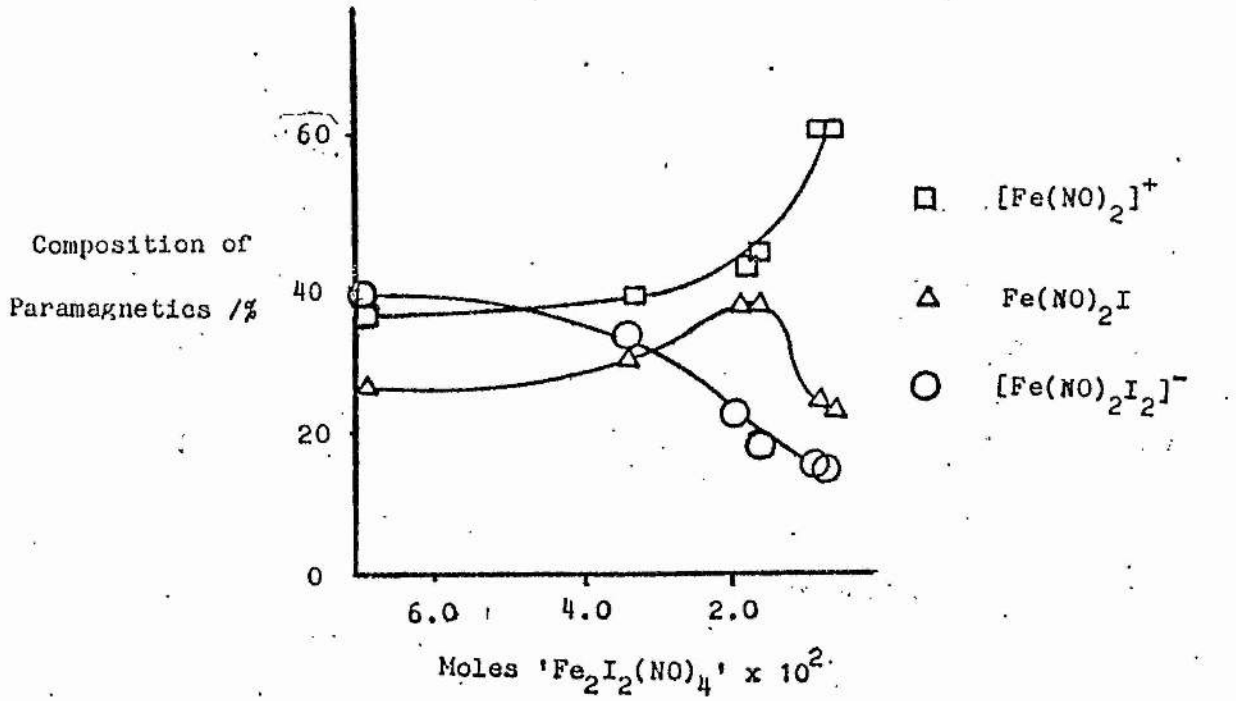


Fig. 5.1; E.p.r. spectrum of $[Fe(NO)_2I_2]^-$, $Fe(NO)_2I$, and $[Fe(NO)_2]^+$.

In the examination of the dissociation of $Fe_2(SR)_2(NO)_4$ in DMF described in chapter 4 two different species were observed, that of $Fe(NO)_2(SR)(DMF)$ and $[Fe(NO)_2(DMF)_2]^+$, with detectable hyperfine coupling in addition to that to the two nitrosyl ligands, to both the protons on the C-S carbon of the alkylthiolate ligand and the unique proton of the coordinated solvent molecules. In an e.p.r. study of iron-halogen-nitrosyls[9] the g-centre for $[Fe(NO)_2]^+$ was determined to be ca. 2.033 in water. It should also be noted that $[Fe(NO)_2(DMF)_2]^+$ generated from $Fe_2(SR)_2(NO)_4$, and $[Fe(NO)_2]^+$ from $Fe_2I_2(NO)_4$, have identical g-centres and essentially identical hyperfine couplings to the nitrogen of the two nitrosyl ligands; this must be coincidental if $[Fe(NO)_2]^+$ is unsolvated in DMF.

Examination of $Fe_2I_2(NO)_4$ over a range of concentrations in DMF showed the spectral composition to be concentration dependent. Solutions of about 10^{-1} M possessed in addition to the quintet of $[Fe(NO)_2]^+$ two other components(fig. 5.1, table 5.1). The first of these has a six line spectrum, each peak being of equal intensity, with a g-centre ca. 2.053 and $A(^{127}I)$:19.2 G. The second has an eleven line spectrum with relative intensities 1:2:3:4:5:6:5:4:3:2:1 with g-centre ca. 2.079 and $A(^{127}I)$:20.6 G. These two spectra are assigned to $Fe(NO)_2I$ and $[Fe(NO)_2I_2]^-$ respectively, the assignment being based on the multiplicity of the ^{127}I spin of 5/2, and comparison with previous assignments of spectra generated from iron(II) salts, nitric oxide and iodide in both aqueous[9] and ethanolic[16] media. For both of the species the line width (ca. 9 G) is too large for resolution of any hyperfine coupling of the



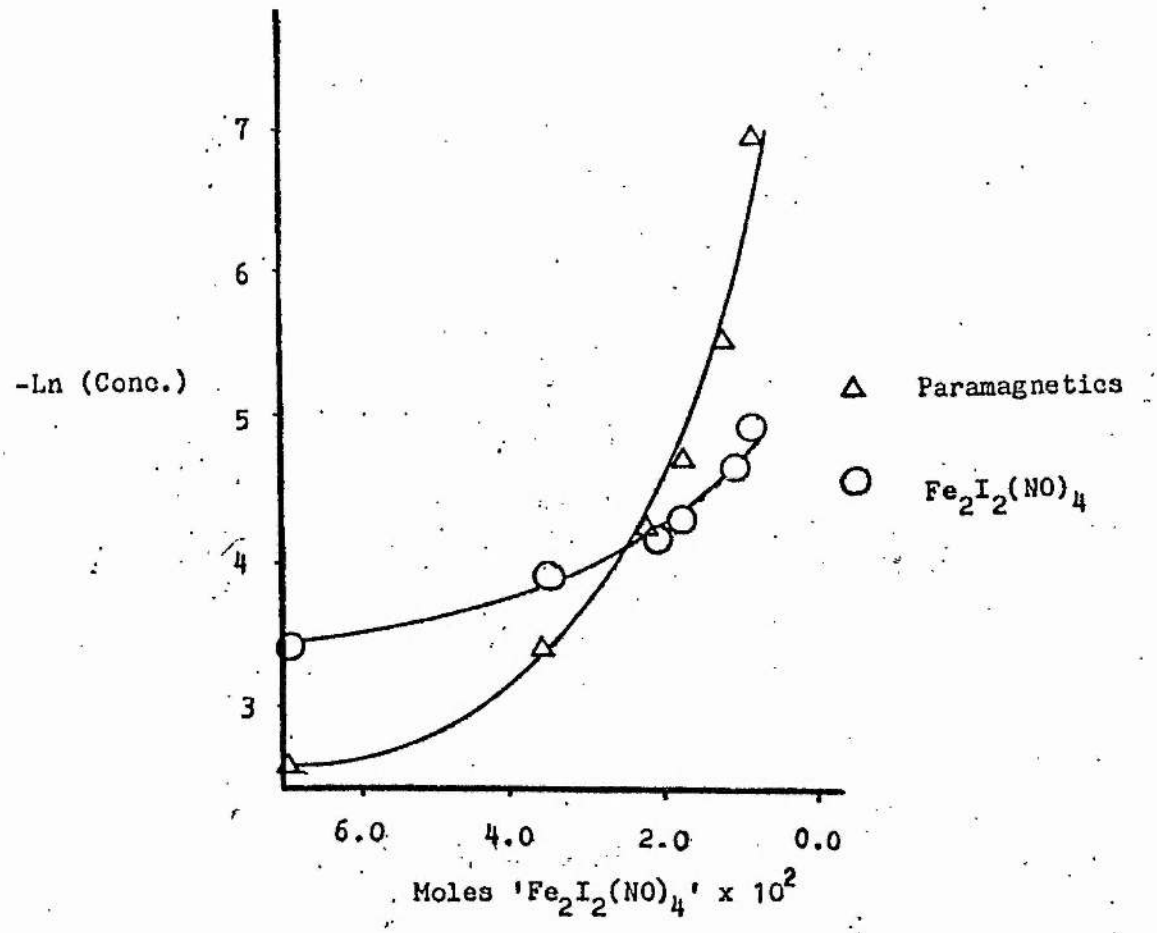


Fig. 5.2 Concentration of species generated from $Fe_2I_2(NO)_4$ in DMF

nitrogens of the nitrosyl ligands; this is consistent with previous observations .

The observation of concentration dependent spectra is consistent with the existence of a series of independent equilibria:

$$2[Fe(NO)_2]^+ + 2I^- \overset{K_1}{\rightleftharpoons} 2[Fe(NO)_2I] \overset{K_2}{\rightleftharpoons} Fe_2I_2(NO)_4$$

$$\overset{K_3}{\rightleftharpoons} [Fe(NO)_2]^+ + [Fe(NO)_2I_2]^-$$

characterised by the equilibrium K_1 - K_3, where

$$K_1 = [Fe(NO)_2I]/[Fe(NO)_2^+][I^-],$$

$$K_2 = [Fe_2I_2(NO)_4]/[Fe(NO)_2I]^2$$

and

$$K_3 = [Fe(NO)_2^+][Fe(NO)_2I_2^-]/[Fe_2I_2(NO)_4].$$

Measurements of the absolute concentrations of the paramagnetic ions by e.p.r. spectroscopy were performed at 240 K for solutions in the concentration range 10^{-1}-10^{-2} mol dm^{-3} of 'undissociated' $Fe_2I_2(NO)_4$ (fig. 5.2). From these results the concentrations of the diamagnetic $Fe_2I_2(NO)_4$ and iodide were calculated by difference. Values for the equilibrium constants K_1-K_3 were determined from the concentrations thus obtained: $\log_{10}K_1$,2.58±0.09; $\log_{10}K_2$,2.71±0.36 and $\log_{10}K_3$,-2.78±0.57.

In addition to the independent equilibria, a series of dependent equilibria exist:

$$[Fe(NO)_2]^+ + 2I^- \xrightleftharpoons{K_4} [Fe(NO)_2I_2]^-$$

$$[Fe_2I_2(NO)_4 \xrightleftharpoons{K_5} 2[Fe(NO)_2]^+ + 2I^-$$

$$2Fe(NO)_2I \xrightleftharpoons{K_6} [Fe(NO)_2]^+ + [Fe(NO)_2I_2]^-$$

characterised by the equilibrium constants K_4-K_6, where

$$K_4 = [Fe(NO)_2I_2^-]/[Fe(NO)_2^+][I^-]^2 = K_1^2K_2K_3,$$

$$K_5 = [Fe(NO)_2^+]^2[I^-]^2/[Fe_2I_2(NO)_4] = (K_1^2K_2)^{-1}$$

and

$$K_6 = [Fe(NO)_2^+][Fe(NO)_2I_2^-]/[Fe(NO)_2I] = K_2K_3.$$

This yields values for K_4-K_6 at 240K of: $\log_{10}K_4$,5.10±0.38; $\log_{10}K_5$,-7.88±0.30 and $\log_{10}K_6$,-0.07±0.22. The precision of the values K_1-K_6 is low since measurement of absolute concentrations by e.p.r. spectroscopy is about ±10%. Precision is further reduced since the three paramagnetic species $[Fe(NO)_2]^+$, $Fe(NO)_2I$ and $[Fe(NO)_2I_2]^-$ demonstrate overlapping spectra in DMF and the concentrations of $Fe_2I_2(NO)_4$ and I^- were determined by difference.

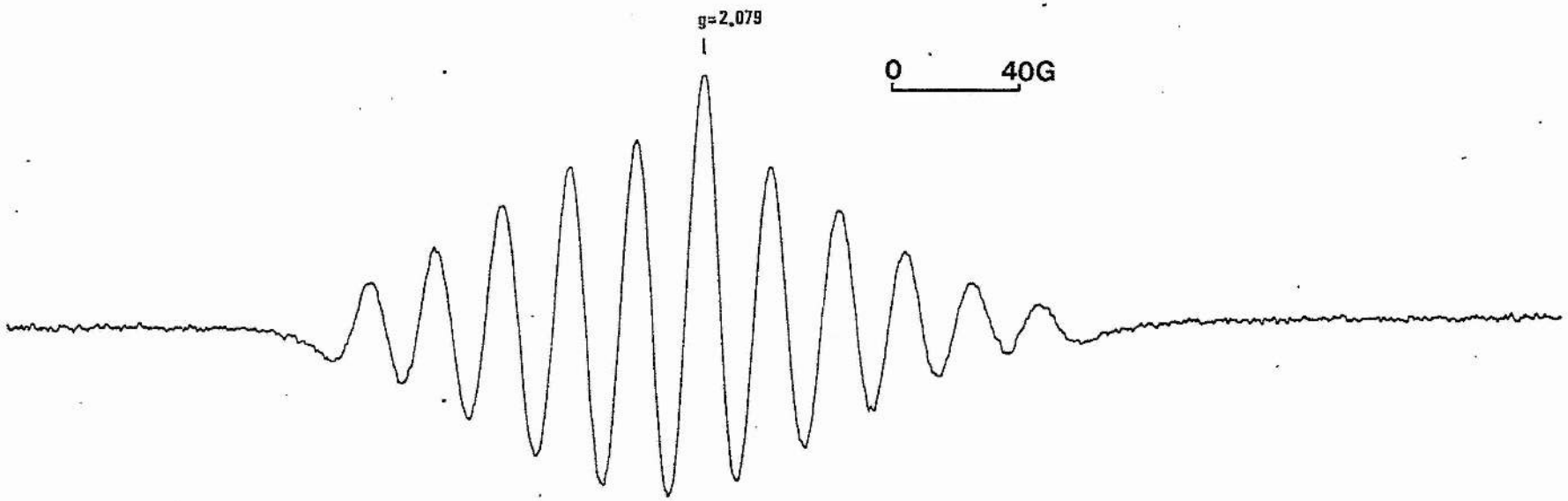


Fig. 5.3; E.p.r. spectrum of $[Fe(NO)_2I_2]^-$.

Table 5.1: E.p.r. parameters for dissociation products of $Fe_2X_2(NO)_4$.

	Species	g	$A(^{14}N)$/G	$A(X)^a$/G
(i) In DMF	$Fe(NO)_2^+$	2.032	2.3	-
	$Fe(NO)_2{}^{35}Cl_2^-$	2.036	2.2	4.7
	$Fe(NO)_2{}^{37}Cl_2^-$	2.036	2.2	4.2
	$Fe(NO)_2Br$	2.037	b	19.2
	$Fe(NO)_2{}^{79}Br_2^-$	2.049	2.5	18.4
	$Fe(NO)_2{}^{81}Br_2^-$	2.049	2.5	20.0
	$Fe(NO)_2I$	2.037	b	19.2
	$Fe(NO)_2I_2^-$	2.079	b	20.6
(ii) In THF	$Fe(NO)_2I$	2.060	b	16.6
	$Fe(NO)_2I_2^-$	2.080	b	20.5
(iii) In H_2O[c]	$Fe(NO)_2^+$	2.033	b	-
	$Fe(NO)_2Cl_2^-$	2.034	b	5.3
	$Fe(NO)_2Br$	2.039	b	19.5
	$Fe(NO)_2Br_2^-$	2.045	b	19.5
	$Fe(NO)_2I$	2.055	b	20.2
	$Fe(NO)_2I_2^-$	2.070	b	20.2

a. $X=^{35,37}Cl(I=3/2)$, $^{79,81}Br(I=3/2)$, $^{127}I(I=5/2)$.

b. Not resolved

c. Data in H_2O from ref. 9.

5.3.2 Solvent Study of $Fe_2I_2(NO)_4$ and its reactions with halides and pseudohalides.

Addition of potassium iodide to a DMF solution of $Fe_2I_2(NO)_4$ (10^{-2} M) yielded a spectrum composed of single detectable paramagnetic species, that of $[Fe(NO)_2I_2]^-$ (fig. 5.3). addition of the iodide affect the equilibria, defined in 5.3;1 by the equilibrium constants K_1-K_6 to favour $[Fe(NO)_2I_2]^-$. Similarly, addition of excess potassium bromide yielded a spectrum composed solely of a septet (fig. 5.4), identifiable as $[Fe(NO)_2Br_2]^-$ the assignment being based on the multiplicity of the two isotopes of bromine ($I(^{79,81}Br) = 3/2$) and comparison with previous assignments of spectra generated from iron(II) salts[9,16], (table 5.1). As with $[Fe(NO)_2I_2]^-$ the line widths are large in comparison with those observed when alkylthiolato ligands are coordinated (cf. chapter 4). However, unlike $[Fe(NO)_2I_2]^-$, resolution of hyperfine coupling to the two nitrogens of the nitrosyls is observed.

Bromine occurs as two equally abundant isotopes, with identical spin ($I = 3/2$). Three isotopic di-bromo species exist in solution: $[Fe(NO)_2{}^{79}Br_2]^-$, $[Fe(NO)_2{}^{79}Br^{81}Br]^-$ and $[Fe(NO)_2{}^{81}Br_2]^-$ in relative abundances 1:2:1. The di-bromo species $[Fe(NO)_2{}^{79}Br_2]^-$ and $[Fe(NO)_2{}^{81}Br_2]^-$ contain a single isotope of bromine and therefore should be observed as a septet. The di-bromo species $[Fe(NO)_2{}^{79}Br^{81}Br]^-$ contains two different isotopes of bromine with A^o_{iso} values differing by 7.8%[17]. If the line widths are very small, then the observed spectrum for the mixed isotopic species will be composed of a quartet of quartets. However, if the line width is too

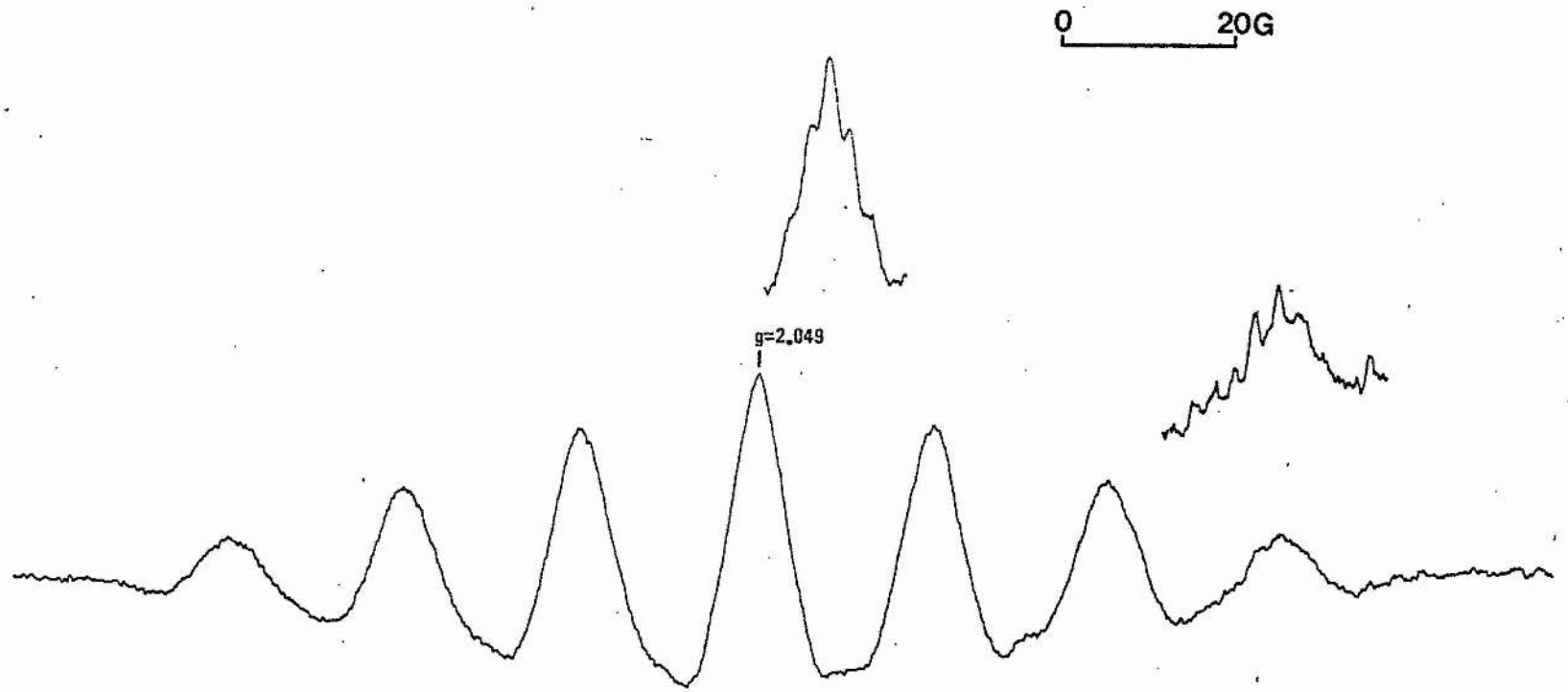


Fig. 5.4; E.p.r. spectrum of $[Fe(NO)_2Br_2]^-$

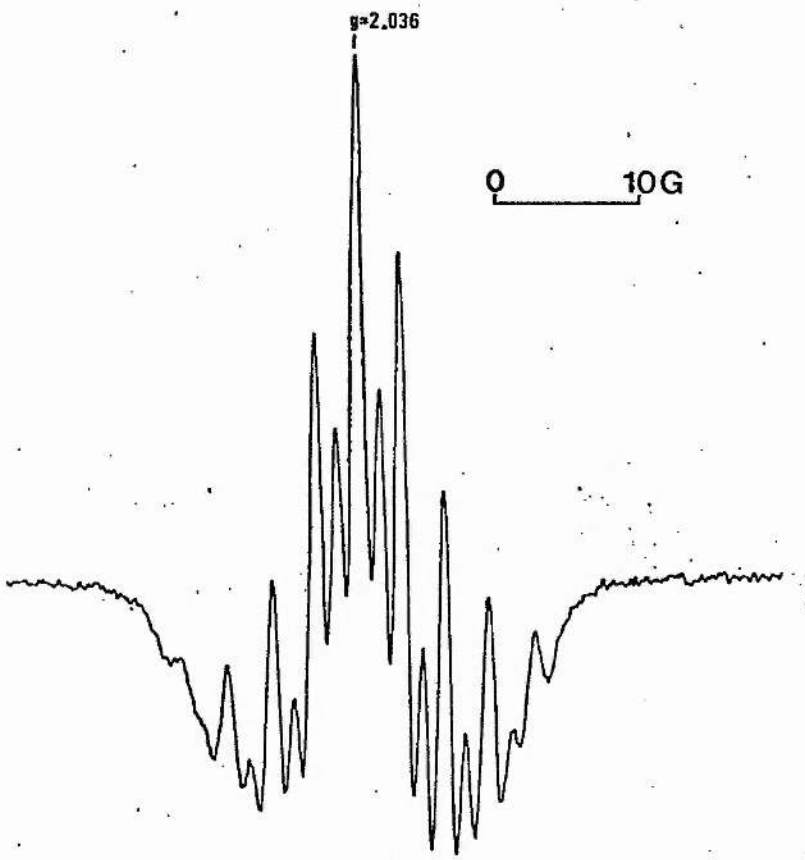


Fig. 5.5; E.p.r. spectrum of $[Fe(NO)_2Cl_2]^-$

large then this species will be observed as a septet. Due to the reduced line widths of $[Fe(NO)_2Br_2]^-$ compared to $[Fe(NO)_2I_2]^-$ nitrogen hyperfine coupling can be resolved. Resolution of the isotopic bromine hyperfine coupling is also achieved, the observed difference between $A(^{79}Br)$;18.4G and $A(^{81}Br)$;20.0G is 8.7% which agrees quite well with the ratio of A^o_{iso} values. ΔA for the two isotopes of bromine is 1.6G; therefore for the separate isotopes to be resolved in $[Fe(NO)_2{}^{79}Br^{81}Br]^-$ line widths of less than 0.2G would be required. This was not obtained and a septet was observed.

In addition to the spectrum of $[Fe(NO)_2Br_2]^-$, a weak quartet assigned to the monobromo species $Fe(NO)_2Br$ was obtained by addition of smaller quantities of bromide to solutions of $Fe_2I_2(NO)_4$ in DMF. Due to poor resolution no hyperfine coupling to nitrogen was resolved. Likewise no isotopic splitting was observed in the bromine quartet. As with the mono iodo species $Fe(NO)_2I$, the magnitude of the halogen's hyperfine coupling is about the same as that observed for the di-halo species.

Addition of excess potassium chloride to a solution of $Fe_2I_2(NO)_4$ yielded a temperature dependent spectrum. At ambient temperature, a single paramagnetic species, that of $[Fe(NO)_2I_2]^-$ was detected. Low temperature examination of the same mixture (205K) yielded a spectrum containing $[Fe(NO)_2Cl_2]^-$ with no $[Fe(NO)_2I_2]^-$ detectable (fig. 5.5). Warming this mixture to 270K resulted in the replacement of the spectrum assigned to $[Fe(NO)_2Cl_2]^-$ by that of $[Fe(NO)_2I_2]^-$. The ready formation of $Fe(NO)_2Br_x$ (x = 1,2) from $Fe_2I_2(NO)_4$ and the observed temperature dependent spectrum of $[Fe(NO)_2Cl_2]^-$ is evidence that, like

alkylthiolato ligands, the halide ions are labile to exchange. The absence of $[Fe(NO)_2]^+$ and $Fe(NO)_2I$ from the observed spectrum can be explained by the substitution of chloride to form $Fe_2Cl_2(NO)_4$ which only ring opens at low temperatures. The absence of any detectable $[Fe(NO)_2I_2]^-$ at low temperatures suggests that the halogen exchange equilibria are temperature dependent.

Like bromine, chlorine occurs as two naturally occurring isotopes, ^{35}Cl and ^{37}Cl, both with I = 3/2 in relative abundance 3:1. Thus three isotopic dichoro species exist in solution: $[Fe(NO)_2{}^{35}Cl_2]^-$, $[Fe(NO)_2{}^{35}Cl{}^{37}Cl]^-$ and $[Fe(NO)_2{}^{37}Cl_2]^-$ in relative abundances 9:6:1. Resolution of the isotopic chlorine hyperfine coupling was achieved. The observed difference between $A(^{35}Cl)$ and $A(^{37}Cl)$, is 0.5G (10%). which agrees with the ratio of the A^o_{iso} values of 10%[17]. In addition to resolution of chlorine isotopic splitting nitrogen hyperfine coupling is also apparent. Unlike solutions produced in ethanolic[16] and aqueous[9] mixtures no $Fe(NO)_2Cl$ was observed.

Addition of potassium fluoride to $Fe_2I_2(NO)_4$ in DMF had no detectable effect on the e.p.r. spectra, even on lowering the temperature to the freezing point of the solvent. Addition of cadmium, silver and thallium fluorides likewise yielded no spectra showing fluorine coupled to $[Fe(NO)_2]^+$ and it must be assumed that the halogen exchange equilibrium strongly favours the iodo complexes.

Assignments of g-centres for $[Fe(NO)_2X_2]^-$ (X = I^-, Br^- and Cl^-) agree quite well with those previously observed for species generated from iron(II) salts, nitric oxide and halide ions[9,16], (table 5.1). Likewise, the hyperfine coupling constants available for comparison[9,16,18] agree reasonably well. Where resolved, the nitrogen hyperfine coupling of the two nitrosyl ligands is of the same magnitude as that observed when alkylthiolato ligands are complexed. The g-centre for these $[Fe(NO)_2L_2]^-$ complexes are variable. The greater the mass of the ligated halogen atoms and their number the greater the shift in g-centre to low field.

Examination of $Fe_2I_2(NO)_4$ in THF (10^{-2} M) yielded a single six line spectrum assignable to $Fe(NO)_2I$. Examination of $Fe_2I_2(NO)_4$ over a range of concentrations in THF yielded no other detectable paramagnetic species. Therefore, unlike solutions in DMF, a single equilibrium equation:

$$Fe_2I_2(NO)_4 \overset{K}{\rightleftharpoons} 2Fe(NO)_2I$$

is sufficient to describe solutions of $Fe_2I_2(NO)_4$ in THF.

In chapter 4, several different mono alkylthiolato substituted complexes, $Fe(NO)_2SR(L)$ (L=solvent) are reported. Except when L=DMF no hyperfine coupling to solvent was detected; this is unsuprising for solvents such as DMSO where, assuming coordination is via the oxygen atom the nearest atom with spin (hydrogen) is separated from the paramagnetic centre by three atoms. However, it is surprising that no

coupling to either nitrogen or hydrogen is resolvable when L=Et_2NH. Although resolvable hyperfine couplings are absent, solvent interactions can be characterised by the solvent dependent g-centre. It is noted above that the g-centre of the di-halo complex $[Fe(NO)_2X_2]^-$ is dependent upon the mass of the substituted halogen. In addition to the mass of the substituted halogen, the g-centre in the mono halo species $Fe(NO)_2X$ is like $Fe(NO)_2SR$ solvent dependent and a similar solvent interaction can be assumed.

On addition of potassium iodide to solutions of $Fe_2I_2(NO)_4$ in THF, the six line spectrum of $Fe(NO)_2I$, is replaced by that of $[Fe(NO)_2I_2]^-$. However, addition of potassium bromide to solutions of $Fe_2I_2(NO)_4$ in THF yielded e.p.r. silent solutions at both low and high temperatures. This addition of bromide to $Fe(NO)_2I$ facilitates halogen exchange to form $Fe(NO)_2Br$, which is in equilibrium with the diamagnetic dimer $Fe_2Br_2(NO)_4$. In solvents such as DMF solvent-solute interactions enhance ring opening of $Fe_2Br_2(NO)_4$ to yield $Fe(NO)_2Br$ and $[Fe(NO)_2Br_2]^-$. THF is a less efficient ring opening solvent than DMF, and examination of $Fe_2(SR)_2(NO)_4$ in THF also yielded e.p.r. silent solutions. This is also found in the study of $Fe_2I_2(NO)_4$ over a range of concentrations in THF, where the concentration of $Fe(NO)_2I$ was found to be about a tenth of that determined in DMF. The solvent and bridging ligand dependence on the equilibrium:

$$Fe_2(NO)_4L_2 \rightleftharpoons 2Fe(NO)_2L$$

is consistent with the magnitude of the Fe-Fe distance. The Fe-Fe distance in $Fe_2I_2(NO)_4$[19] is 3.05Å, whilst in $Fe_2(SEt)_2(NO)_4$[20] it is

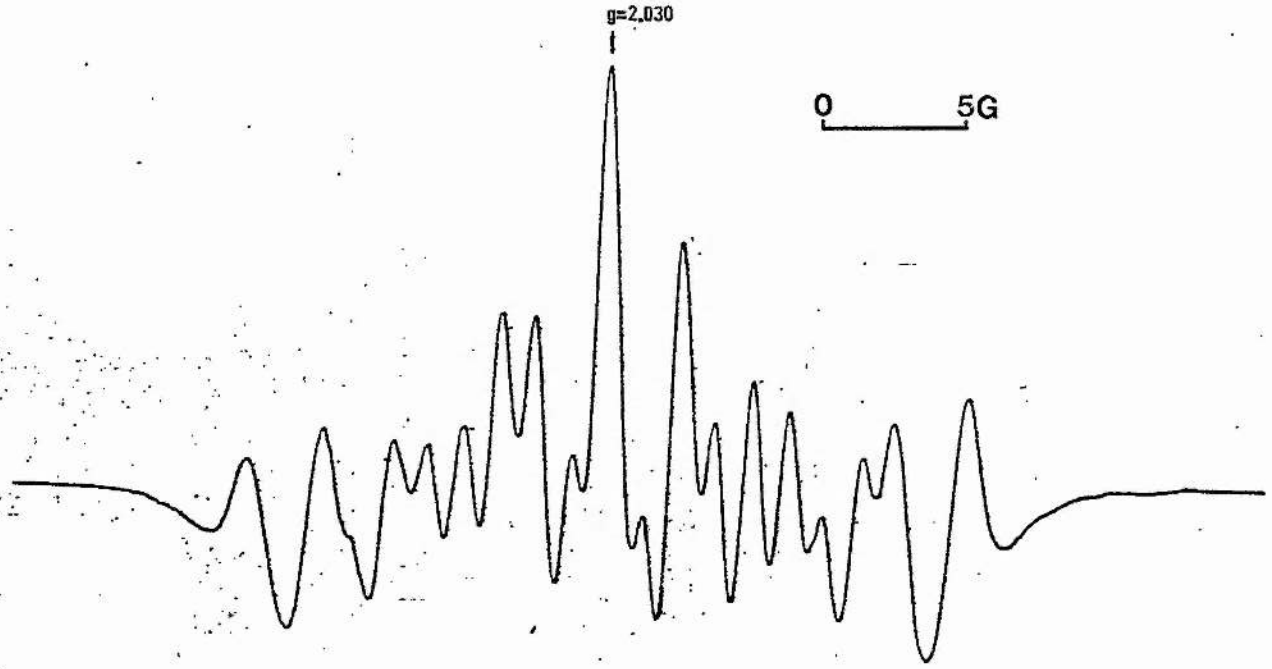


Fig. 5.6; E.p.r. spectrum of $[Fe(NO)_2(NCO)_2]^-$

reduced by 11% to 2.72Å. The bond angles Fe-X-Fe in these two compounds are essentially identical, and if this is assumed to be true for $Fe_2Br_2(NO)_4$ also, then by application of a reasonable estimate for the Fe-Br bond distance of 2.38Å[21] a value of about 2.8Å for the Fe-Fe distance is obtained. The diamagnetism[19] of the dimeric complex $Fe_2X_2(NO)_4$, has been explained as being due to the existence of a direct Fe-Fe bond[22] and hence the greater this distance, the more susceptible the complex will be to dissociation.

Addition of the pseudohalogens NCO^-, NCS^-, and $NCSe^-$ to DMF solutions of $Fe_2I_2(NO)_4$ resulted in the generation of new e.p.r. spectra. Addition of NCS^- yielded the complex $[Fe(NO)_2(NCS)_2]^-$ identical to that previously observed[9] in $Fe(II)/NCS^-/NO$ reactions. Addition of NCO^- yielded the analogous complex $[Fe(NO)_2(NCO)_2]^-$ (g=2.030, $A(^{14}N)$= 2.6G (2xNCO), 1.8G (2xNO) (fig. 5.6). Addition of selenocyanate (NCSe) yielded a complex weak spectrum which could not be unambiguously assigned.

5.3.3 Conversion of $Fe_2I_2(NO)_4$ into $Fe_2(SR)_2(NO)_4$.

Rauchfuss and Weatherill[1] have shown that addition of alkyl thiols and a base to THF solutions of the μ_2-iodo complex $Fe_2I_2(NO)_4$ yield $Fe_2(SR)_2(NO)_4$ in a preparatively useful procedure:

$$Fe_2I_2(NO)_4 + 2RSH + 2Et_3N \longrightarrow Fe_2(SR)_2(NO)_4 + Et_3NH^+I^-.$$

In this section an e.p.r. examination of this interconversion of

$Fe_2I_2(NO)_4$ into $Fe_2(SR)_2(NO)_4$ is reported.

Examination of solutions of $Fe_2I_2(NO)_4$ in THF showed the existence of a dimer/monomer equilibrium:

$$[Fe(NO)_2I]_2 \rightleftharpoons 2[Fe(NO)_2I]$$

Addition of the base, triethylamine, to THF solutions of $Fe_2I_2(NO)_4$ yielded e.p.r. spectra similar to those of the μ_2-iodo complex in DMF:

$$[Fe(NO)_2I]_2 \rightleftharpoons 2Fe(NO)_2I \longrightarrow [Fe(NO)_2I_2]^- + Fe(NO)_2I + [Fe(NO)_2I_2]^-$$

E.p.r. examination of $Fe_2I_2(NO)_4$ in Et_3N yielded a spectrum composed of a single paramagnetic species, that of $[Fe(NO)_2(NEt_3)_2]^+$ (g=2.030, A(N)=4.7G, A(N)=2.2G). The observation of a disolvo complex is noteworthy since it demonstrates that the nature of the bridging ligands affect the solvo complex. In chapter four it is shown that $Fe_2(SR)_2(NO)_4$ forms mono-solvo complexes ($Fe(NO)_2(SR)(Solv)$) in aliphatic amines. This observation suggests that the alkylthiolato group bonds stronger to $[Fe(NO)_2]^+$ than iodide.

What appears to happen on addition of triethylamine to THF solutions of $Fe_2I_2(NO)_4$ is that the iodide coordinated to $Fe(NO)_2I$ is displaced to yield $[Fe(NO)_2]^+$ coordinated to Et_3N, the displaced iodide then combines with $Fe(NO)_2I$ to yield $[Fe(NO)_2I_2]^-$.

$$Fe(NO)_2I \xrightarrow{Et_3N} [Fe(NO)_2(NEt_3)_2]^+ + I^-$$

$$Fe(NO)_2I + I^- \longrightarrow [Fe(NO)_2I_2]^-$$

$$[Fe(NO)_2I_2]^- \xrightarrow{Et_3N} [Fe(NO)_2(NEt_3)_2]^+ + 2I^-$$

Continued addition of triethylamine displaces the iodine from the di iodo complex to yield $[Fe(NO)_2(NEt_3)_2]^+$.

Addition of a thiol (chosen throughout as i-propyl mercaptan for simplified spectral assignment, since this thiol contains only a single α-proton) to solutions of $Fe_2I_2(NO)_4$ in THF/Et_3N mixtures caused the spectra of $[Fe(NO)_2I_2]^-$, $Fe(NO)_2I$ and $[Fe(NO)_2]^+$ to be replaced by that composed of two paramagnetic complexes. The first of these is a dinitrosyl species identifiable as that of $[Fe(NO)_2(SR)_2]^-$ and the second, a mono-nitrosyl species with no coupling to hydrogen resolved (g=2.040; $A(^{14}N)$=13.5G). In chapter 4 the reversible equilibrium:

$$2[Fe(NO)_2(SR)_2]^- \rightleftharpoons [Fe(NO)_2SR]_2 + 2RS^-$$

is reported, and the formation of the dithiolato complex can thus be described:

$$[Fe(NO)_2(NEt_3)_2]^+ + Fe(NO)_2I(NEt) + [Fe(NO)_2I_2]^-$$

$$\downarrow \text{RSH}$$

$$[Fe(NO)_2(SR)_2]^-$$

$$\Downarrow$$

$$[Fe(NO)_2SR]_2$$

The identification of the second paramagnetic species is more difficult; its spectrum is composed of three equivalent peaks with no other resolved hyperfine coupling. This suggests that the species is a mono-nitrosyl complex, but full spectral assignment is prevented due

to the absence of any other resolved hyperfine couplings in this unstable species. In the preparative conversion of $Fe_2I_2(NO)_4$ into $Fe_2(SR)_2(NO)_4$ it appears that the mono-nitrosyl species is formed in only small quantities, since the sole species detected in the recrystallised product is the diamagnetic dimer, $Fe_2(SR)_2(NO)_4$.

Addition of RSH to a THF solution of $Fe_2I_2(NO)_4$, before the addition of Et_3N, resulted in a different spectrum from that observed in the presence of base. Addition of base caused the replacement of the six line spectrum by that of the eleven line spectrum of $[Fe(NO)_2I_2]^-$. This observation can be interpreted as resulting from displacement by the alkylthiolate of iodide to yield $Fe(NO)_2SR$ which immediately dimerizes to yield the diamagnetic $Fe_2(SR)_2(NO)_4$. The resulting displaced iodide combines with unreacted $Fe(NO)_2I$ to yield the di-iodo species $[Fe(NO)_2I_2]^-$:

$$Fe(NO)_2I + RSH \longrightarrow Fe(NO)_2SR + H^+ + I^-$$

$$2Fe(NO)_2SR \longrightarrow Fe_2(SR)_2(NO)_4$$

$$Fe(NO)_2I + I^- \longrightarrow [Fe(NO)_2I_2]^-$$

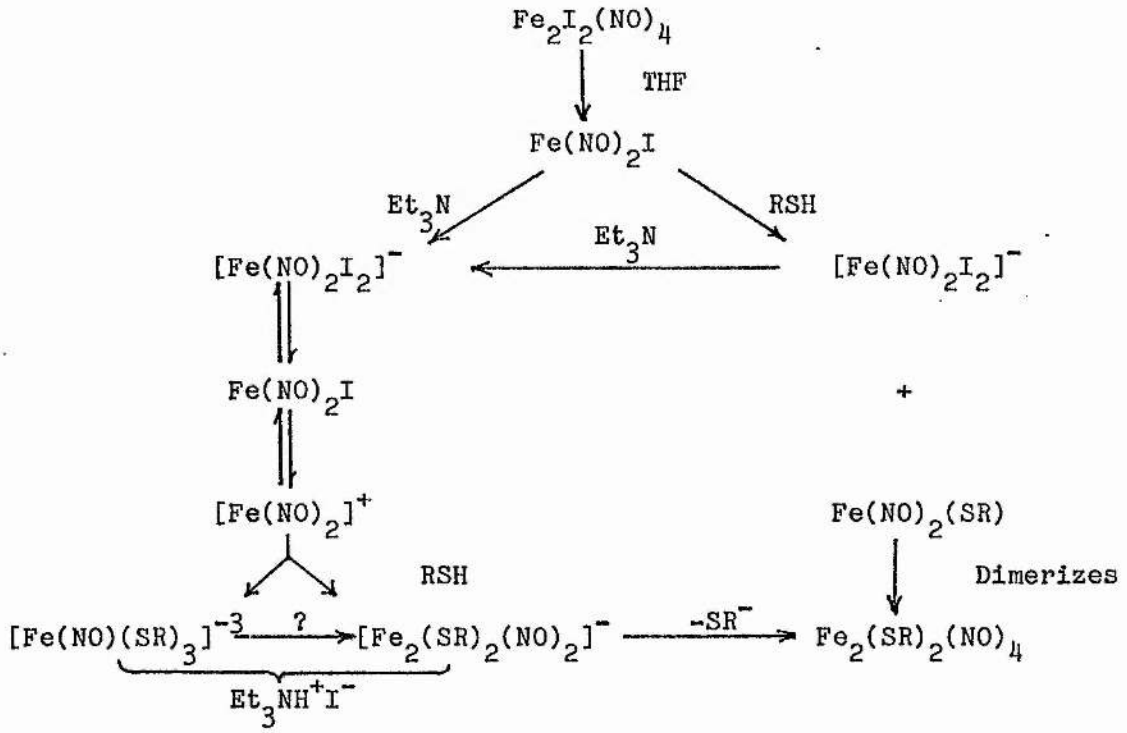
According to Burlamacchi and coworkers[9] the formation of the di-iodo species is enhanced by acidification, which in this case results from the addition of the thiol. Addition of Et_3N to THF solutions of $Fe_2I_2(NO)_4$ in the presence of an excess of RSH yielded diamagnetic solutions. Addition of Et_3N to mixtures containing insufficient thiol for complete stoichiometric conversion of $Fe_2I_2(NO)_4$ caused

conversion of the di-iodo species $[Fe(NO)_2I_2]^-$ into $[Fe(NO)_2(NEt_3)_2]^+$ as the base displaces the coordinated iodide.

$$[Fe(NO)_2I_2]^- \xrightarrow{Et_3N} [Fe(NO)_2(NEt_3)_2]^+$$

In contrast to $Fe_2I_2(NO)_4$, the alkyl esters of $Fe_2(SR)_2(NO)_4$ undergo very little dissociation, even in strongly polar solvents. THF solutions of $Fe_2(SR)_2(NO)_4$ are e.p.r. silent and it can be assumed therefore that dissociation in pure THF can be ignored. It was found that reaction of $Fe_2I_2(NO)_4$ with a 100-fold excess of i-PrSH in THF yielded, even in the absence of any amine, $Fe_2(SPr^i)_2(NO)_4$ in 93% yield, thus supporting the above equations.

A sequence of equations can therefore be suggested for the conversion of $Fe_2I_2(NO)_4$ to $Fe_2(SR)_2(NO)_4$ in THF solutions:



with the exception of $Fe(NO)_2SR$ all the paramagnetic species in this scheme were detected by e.p.r. spectroscopy. Triethylammonium iodide is insoluble in THF, and it appears that its precipitation is the driving force to the formation of $Fe_2(SR)_2(NO)_4$ in preparatively useful yields when stoichiometric quantities of reactants are employed.

The sequence of reactions listed above is at least partially reversible, in DMF. Addition of iodide to $Fe_2(SR)_2(NO)_4$ in DMF yielded $[Fe(NO)_2I_2]^-$ as the sole detectable paramagnetic species, likewise addition of bromide yielded $[Fe(NO)_2Br_2]^-$. Addition of chloride appeared to have no effect on the observed spectrum, the spectrum even at low temperatures being composed solely of a mixture of $Fe(NO)_2(SR)(DMF)$ and $[Fe(NO)_2(DMF)_2]^+$.

The generation of paramagnetic mono-iron fragments from $Fe_2X_2(NO)_4$ is coupled with a change in colour from red to green. This colour, and hence the composition of the solution is easily adjusted by the addition of non-polar solvents, resulting in the formation of diamagnetic red solutions. Subsequent addition of polar solvents regenerates the green solution containing mono-iron fragments. The implication of this observation is that it suggests a synthetic route to new diamagnetic iron-nitrosyl complexes from preformed complexes:

$$\left.\begin{matrix} Fe_2I_2(NO)_4 \\ \\ Fe_2(SMe)_2(NO)_4 \end{matrix}\right\} \xrightarrow[X^-]{DMF} Fe(NO)_2X_2^- \xrightarrow{Toluene} Fe_2X_2(NO)_4$$

This will be the subject of investigation by coworkers.

5.4 References.

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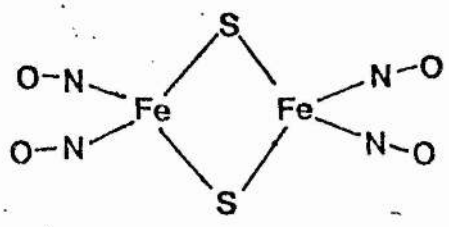


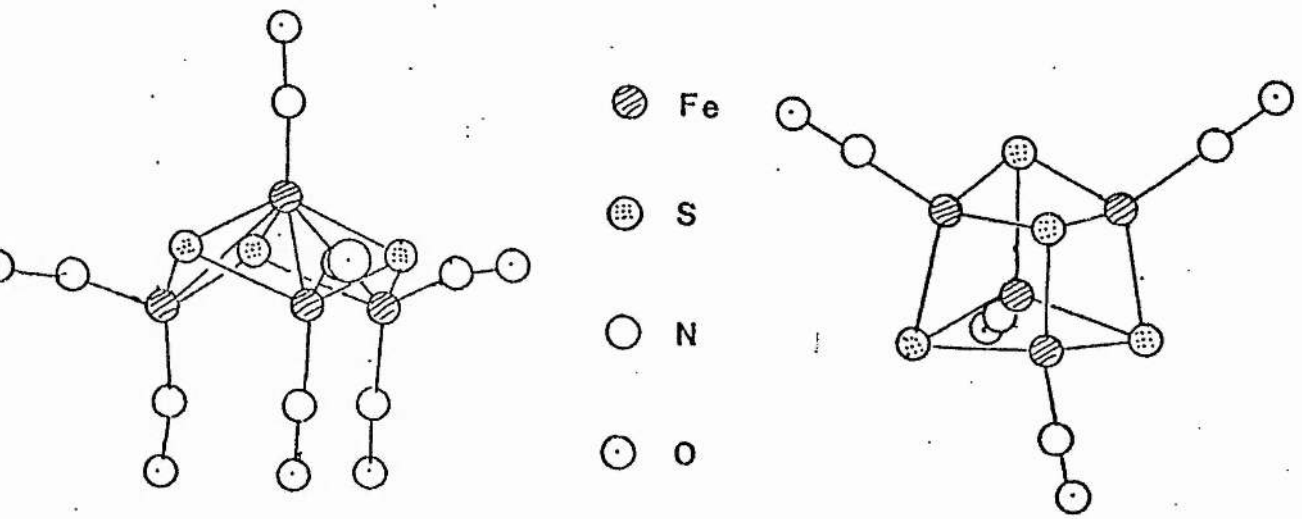


Fig. 6.1; Structures of $[Fe_4S_3(NO)_7]^-$, $[Fe_2S_2(NO)_4]^{-2}$, and $Fe_4S_4(NO)_4$.

CHAPTER SIX

INTERCONVERSION OF IRON-CHALCOGEN-NITROSYLS.

6.1 Introduction.

In chapters 4 and 5 the lability of the bridging ligands in $Fe_2X_2(NO)_4$ (X=halogens,RS^-) to exchange is reported.

$$Fe_2X_2(NO)_4 \underset{2X}{\overset{2L}{\rightleftharpoons}} Fe_2L_2(NO)_4$$

In this chapter the results of an investigation into the reactions of both $[Fe_4S_3(NO)_7]^-$ and $Fe_4S_4(NO)_4$ are reported and compared to those obtained for $Fe_2(SR)_2(NO)_4$, reported in chapter 4.

The three basal iron atoms in $[Fe_4S_3(NO)_7]^-$ (fig 6.1) have been described as being analogous to the iron atoms in $[Fe_2S_2(NO)_4]^{-2}$ and have been assigned the same formal oxidation state of $-1(d^9)^1$. The apical iron in the $[Fe_4S_3(NO)_7]^-$ complex has been compared[1] to a corner of the cubane analogue $Fe_4S_4(NO)_4$, and is thus assigned a formal oxidation state of $+1(d^7)$. The close analogy between these three may result in the compounds' demonstrating similar chemistries. The tetra-iron complex $[Fe_4S_3(NO)_7]^-$ is readily converted into the dianion $[Fe_2S_2(NO)_4]^{-2}$ by reflux in aqueous base[2,3], whilst reflux with sulphur yields the cubane analogue $Fe_4S_4(NO)_4$[4].

$$Fe_4S_4(NO)_4 \xleftarrow{S} [Fe_4S_3(NO)_7]^- \xrightarrow{OH^-} 3/2[Fe_2S_2(NO)_4]^{-2} + [Fe(NO)]^{+2}$$

These reactions illustrate that these iron-nitrosyl complexes are capable of interconversion.

6.2 Experimental.

6.2.1 Instruments and Materials.

Literature methods were employed for the preparation of $Fe_2I_2(NO)_4$[5], $[Fe(CO)_3(NO)](PPN)$[6] and $Fe(NO)(S_2CNMe_2)_2$[7]. $Fe_2(SR)_2(NO)_4$ was prepared either from the carbonyl as describe in chapter 2 or from $Fe_2I_2(NO)_4$ as described in the literature[8]. $Fe_4S_4(NO)_4$ was prepared as described in chapter 4 from $[Fe_4S_3(NO)_7]^-$. All compounds synthesised in the exchange reactions were characterised by comparison with analytical data of authentic samples. All chemicals employed were Analar grade or the purest commercially available. ^{15}N labelled compounds were prepared by modification of the procedure listed, using 99% $Na[^{15}NO_2]$ (purchased from MSD Isotopes, Inc.).

All manipulations were performed in an atmosphere of dry nitrogen: all organic solvents were the purest commercially available, dried by conventional methods, and purged with dry nitrogen before use.

Second derivative e.p.r. spectra were recorded for solutions generally of about 10^{-2}mol dm^{-3} , usually at 240K, in 1 mm quartz capillaries using a Bruker ER 200D spectrometer: di-t-butyl nitroxide was used as the standard for the measurement of line positions. Hyperfine coupling constants for nitrogen are quoted for ^{14}N unless otherwise stated. Mass spectra were obtained using an AEI MS 902. ^{1}H n.m.r. spectra were recorded on a Bruker WP-80 instrument. I.r. spectra were recorded on a Perkin-Elmer 1330 spectrometer: u.v. spectra were recorded on a Pye-Unicam SP8-100 spectrometer.

6.2.2 Preparation and reactions of $Na[Fe_4S_3(NO)_7]$

Roussins Black salt, $[Fe_4S_3(NO)_7]^-$ was prepared by the following adaption of the method given by Brauer[9]. Sodium nitrite (8.0g) and sodium sulphide (11.3g) were dissolved in water (80 ml). This mixture was heated to 100°C and $FeSO_4.7H_2O$ (20.0g) in water (160 ml) was added; the resultant black mixture was evaporated to dryness. The resulting solid was extracted with acetone, and the extract was filtered through hyflo supercell and evaporated yielding about 3g of crude $[Fe_4S_3(NO)_7]Na$. The compound was best recrystallised from water to yield black needles. Analysis. I.r. ν(N-O)/cm^{-1} 1790m, 1730s, 1690m (lit.[10,11] 1790m, 1730s, 1690m). U.v. λ /nm (/mol $dm^{-3}cm^{-1}$) 560 (2400), 350 (15400), 260 (26700) T.l.c.;single spot moving with solvent front as a brown/black streak in methanol or acetone on a silica plate, non mobile in either CH_2Cl_2 or petrol.

Reactions.(a) With MeSNa. To $Na[Fe_4S_3(NO)_7]$ (0.10g) in DMF (30 ml) was added MeSNa (0.10g). The mixture was stirred under nitrogen for one hour and then diluted with 50ml of CH_2Cl_2. The solution was washed with water (4 x 250 ml), filtered and dried over $MgSO_4$. The solution was evaporated to small volume, and methanol was added to precipitate the product, $Fe_2(SMe)_2(NO)_4$, isolated in 46% purified yield, calculated on the basis of $Fe(NO)_2$ fragments. Analysis. I.r.: $\nu(NO)/cm^{-1}$ 1815w, 1780s, 1750s. (lit. 1775, 1750, 1730[12]; 1778, 1755[13]). Mass spectrum: M/z 326 (molecular ion); 296, 266, 236, 206 (sequential loss of 4 NO); 191, 176 (sequential loss of 2 Me)[14]. ^1H n.m.r. in $CDCl_3$ 2.83 p.p.m. (lit.[12] 2.8 p.p.m.). T.l.c.;single red spot Rf=0.7 on 0.25 mm silica in 40/60 petroleum ether.

(b) With Me_2NCS_2Na. To a solution of $Na[Fe_4S_3(NO)_7]$ (0.50g) in water (400 ml) was added NaOH (2g) and Me_2NCS_2Na (2g). The mixture was stirred for an hour then quenched by addition of CH_2Cl_2 (100ml). The organic layer was washed, dried over Na_2SO_4 , and then evaporated to dryness. Repeated extraction of the aqueous layer with further CH_2Cl_2, followed by washing and drying yielded further portions of solid material. The combined solids were recrystallised from CH_2Cl_2/CH_3OH to yield $Fe(NO)(S_2CNMe_2)_2$ (1.03g: 88% yield based upon total iron, 354% based upon apical iron). Analysis; I.r. $\nu(NO)/cm^{-1}$ 1690s (lit[15]1690). T.l.c:single green spot moving with solvent front on 0.25mm silica in CH_2Cl_2. E.p.r.; g=2.038, $A(^{14}N)$=13.2 (lit[15] g=2.038, $A(^{14}N)$=14.4G).

(c)Preparation of $(PPN)_2[Fe_2S_2(NO)_4]$. To a solution of $Na[Fe_4S_3(NO)_7]$ (0.10g) in water (100 ml) was added NaOH (0.5g): the mixture was refluxed under nitrogen for 15 minutes before addition of [PPN]Cl (2g) dissolved in the minimum volume of warm water. The whole mixture was cooled and extracted with CH_2Cl_2 (2 x 100 ml). The extract was filtered, and washed with water (2 x 100 ml), and dried over $MgSO_4$. The volume was reduced somewhat and the product precipitated by the addition of cold petrol. Yield 0.031g (6.7% based upon total iron, 7.5% based upon NO). Analysis: $\nu(NO)/cm^{-1}$ 1815w, 1780s, 1750s. Elemental Analysis obtained (calc.) C;40.64% (40.48%), H; 2.81% (2.83%), N; 10.47% (10.49%).

6.2.3 Reactions of $Fe_4S_4(NO)_4$.

(a) With Me_2NCS_2Na. Me_2NCS_2Na (0.27g) was added to a solution of $Fe_4S_4(NO)_4$ (0.10g) in DMF (20 ml). The mixture was stirred at room temperature, under nitrogen, during two hours, and then diluted with 50 ml of CH_2Cl_2. The resulting solution was washed with water (4 x 500 ml), filtered, and dried over $MgSO_4$. The solution was reduced to small volume, and ice cold methanol added to precipitate the product, $Fe(NO)(S_2CNMe_2)_2$, isolated in 94% purified yield.

(b) With MeSNa. MeSNa (0.70g; 10 mmol) was added to a stirred solution of $Fe_4S_4(NO)_4$ (0.47g; 1.0 mmol) in DMF (20 ml). The mixture was

refluxed under nitrogen during 2 hours, and then cooled. Toluene (100 ml) was added dropwise to the green solution, via a pressure-equalized dropping funnel, and the resulting red solution was filtered through a 1 cm depth bed of hyflo, and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (30 ml), and washed with water (10 x 200 ml): the organic layer was dried over $MgSO_4$. The solution was reduced to small volume, and the product precipitated by addition of ice cold methanol. The product, $Fe_2(SMe)_2(NO)_4$ (0.040g; 0.13 mmol; 13%) was isolated by filtration and dried in vacuo.

6.2.4 Reactions of $(Pr^iO)_2PS_2Na$

(a) With $Na[Fe_4S_3(NO)_7]$. To a solution of $Na[Fe_4S_3(NO)_7]$ (0.30g) in DMF (50 ml) under nitrogen was added 1.0g of $(Pr^iO)_2PS_2Na$. The mixture was stirred for 10 hours, and then reduced to solid. This solid was dissolved in CH_2Cl_2 (50 ml) and the solution was washed with water, and dried over $MgSO_4$. Removal of the solvent gave a very labile black solid, having ν(NO) ($CHCl_3$ solution), 1800 cm^{-1} (sharp and strong absorption). All attempts to purify this material, under nitrogen, proved unsuccessful.

(b)With $Fe_2I_2(NO)_4$. Substitution of $Fe_2I_2(NO)_4$ for $Na[Fe_4S_3(NO)_7]$ yielded the same material as before: no successful purification was achieved.

In $CHCl_3$, very dilute solutions of this black solid yielded e.p.r. spectra indicative of the presence of two species, characterised by g=2.033, $A(^{14}N)$=2.3G (2N) or $A(^{15}N)$=3.2G (2N) and g=2.030, $A(^{14}N)$=2.2G (1 N) or $A(^{15}N)$=3.1G (1 N) respectively. Identical spectra were obtained from the reaction of $(Pr^iO)_2PS_2Na$ with $Fe_4S_4(NO)_4$, $Fe_2I_2(NO)_4$, $Na[Fe_4S_3(NO)_7]$, $Fe_2(SMe)_2(NO)_4$, and $Fe_2(SP^i)_2(NO)_4$.

6.2.5 Reactions of $Fe(NO)(S_2CNMe_2)_2$.

(a)With Na_2S. $Fe(NO)(S_2CNMe_2)_2$ (0.30g) was dissolved in 1:1 v/v DMF/H_2O (150 ml). An approximately 10-fold excess of Na_2S was added, and the mixture was refluxed under nitrogen for 60 hours. The solution was cooled, diluted with 1 dm^3 water, filtered, and washed with CH_2Cl_2 (8 x 100 ml). The remaining aqueous layer was evaporated to dryness, and the residue dissolved in ether (100 ml): the ether layer was washed with water (4 x 250 ml), and then dried over $MgSO_4$. Removal of the solvent yielded 0.015g of $Na[Fe_4S_3(NO)_7]$ (11% yield based upon iron, 18% based upon nitrosyl groups).

(b)With MeSNa. A solution of $Fe(NO)(S_2CNMe_2)_2$ (1.00g; 3.1 mmol) and MeSNa (2.0g; 28.6 mmol) in DMF (20 ml) was refluxed during two hours under nitrogen. The resulting mixture was cooled and diluted with toluene (100 ml). This mixture was reduced to dryness, the residue

was dissolved in CH_2Cl_2 (30ml) and the resulting solution was washed with water (10 x 200 ml). the organic solution was dried over $MgSO_4$ and evaporated to small volume. This solution was applied to a 1.2m x 2.5 cm dry silica chromatography column: a red product $Fe_2(SMe)_2(NO)_4$ was eluted with methanol/CH_2Cl_2 (20:1 v/v), and isolated in 24% purified yield.

6.2.6 Reactions of $(PPN)[Fe(CO)_3(NO)]$.

(a)With MeSNa. To a stirred solution of $(PPN)[Fe(CO)_3(NO)]$ (1.00g; 1.40 mmol) in DMF (20 ml) was added a large excess (2.0g; 28.6 mmol of MeSNa). The mixture was refluxed under nitrogen for 2 hours, cooled, and filtered through hyflo. After evaporation to dryness, the residue was dissolved in CH_2Cl_2 (30 ml) and the resulting solution was washed with water (10 x 200 ml). The organic solution was dried over $MgSO_4$ and evaporated to small volume. This solution was applied to a 1.2 m x 2.5 cm silica dry chromatography column: a red product, $Fe_2(SMe)_2(NO)_4$ was eluted with methanol/CH_2Cl_2 (20:1 v/v), and isolated in 78% purified yield.

(b)With sulphur. $(PPN)[Fe(CO)_3(NO)]$ (1.63g) and elemental sulphur(1.5g) were dissolved in toluene (200 ml). The mixture immediately turned black, and examination by i.r. spectroscopy and t.l.c. of an aliquot removed from the fresh mixture revealed the presence of $[Fe_4S_3(NO)_7]^-$. The mixture was then refluxed under

nitrogen for 20 hours, and then evaporated to dryness. The residue was repeatedly extracted with CH_2Cl_2, and the organic solution reduced to small volume. The product was precipitated by addition of methanol: t.l.c., and u.v. and i.r. spectroscopy showed the product to consist solely of $(PPN)[Fe_4S_3(NO)_7]$ (yield 84% based upon NO). Prolonged reflux (7 days) of $(PPN)[Fe_4S_3(NO)_7]$ with an excess of sulphur in toluene, caused no detectable conversion to $Fe_4S_4(NO)_4$.

6.3 Results and Discussion.

6.3.1 Reactions of Roussin's Black Salt.

Roussin observed[16] that refluxing the diamagnetic $[Fe_4S_3(NO)_7]^-$ in aqueous base yielded a red solution. This has been identified[2,3] as being due to the formation of the diamagnetic dianion $[Fe_2S_2(NO)_4]^{-2}$, isolable either as a salt[2,3] or by alkylation with RI as $Fe_2(SR)_2(NO)_4$[17]. The formation of $[Fe_2S_2(NO)_4]^{-2}$ from $[Fe_4S_3(NO)_7]^-$ can be formally described as the abstraction of $[Fe(NO)_2S]^-$ groups from $[Fe_4S_3(NO)_7]^-$, which then dimerise to yield $[Fe_2S_2(NO)_4]^{-2}$. Extraction and dimerisation of three $[Fe(NO)_2S]^-$ units in $[Fe_4S_3(NO)_7]^-$ leaves the apical $[Fe(NO)]^{2+}$ which will be paramagnetic if the iron's oxidation state, formally described as $+1(d^7)$, is retained. Aqueous solutions of $[Fe_4S_3(NO)_7]^-$ at neutral pH are e.p.r. silent, but in alkaline solution a weak 3-line e.p.r. spectrum was observed (g=2.027, A(N)=4.7G). The intensity of this spectrum was found, as previously observed[18], to increase with an increase in pH, but at any pH, the intensity decreased with time. The

observed triplet can be assigned to a single nitrogen (I=1) coupling to the paramagnetic centre, and this spectrum is assigned to the fragment $[Fe(NO)]^{+2}$, from the apical site in $[Fe_4S_3(NO)_7]^-$.

$$[Fe_4S_3(NO)_7]^- \xrightarrow{OH^-} 3/2\ [Fe_2S_2(NO)_4]^{-2} + [Fe(NO)]^{+2}$$

It can be inferred from the absence of any paramagnetic di-nitrosyl complex in the e.p.r. examination that the equilibrium (equation 1)

$$2[Fe(NO)_2S]^- \rightleftharpoons [Fe_2S_2(NO)_4]^{-2} \qquad (1)$$

strongly favours the dimer in aqueous base. In the study of the alkyl analogues of $Fe_2(SR)_2(NO)_4$ in DMF reported in chapter 4 it was found that equilibrium (2)

$$[Fe(NO)_2(Solv.)_2]^+ + Fe(NO)_2(SR)(Solv.) \rightleftharpoons Fe_2(SR)_2(NO)_4 \qquad (2)$$

lies further to the left than equilibrium (1).

The differences between the monomer/dimer equilibrium between DMF and water suggests that DMF might be a better solvent for generating mono-iron fragments, in particular for generating '$Fe(NO)_2$' complexes. Solutions of $[Fe_4S_3(NO)_7]^-$ in DMF were found, unlike their counterparts in distilled water, to yield very weak and complex e.p.r. spectra indicative of the presence of at least three paramagnetic species, but these spectra were too poorly resolved for

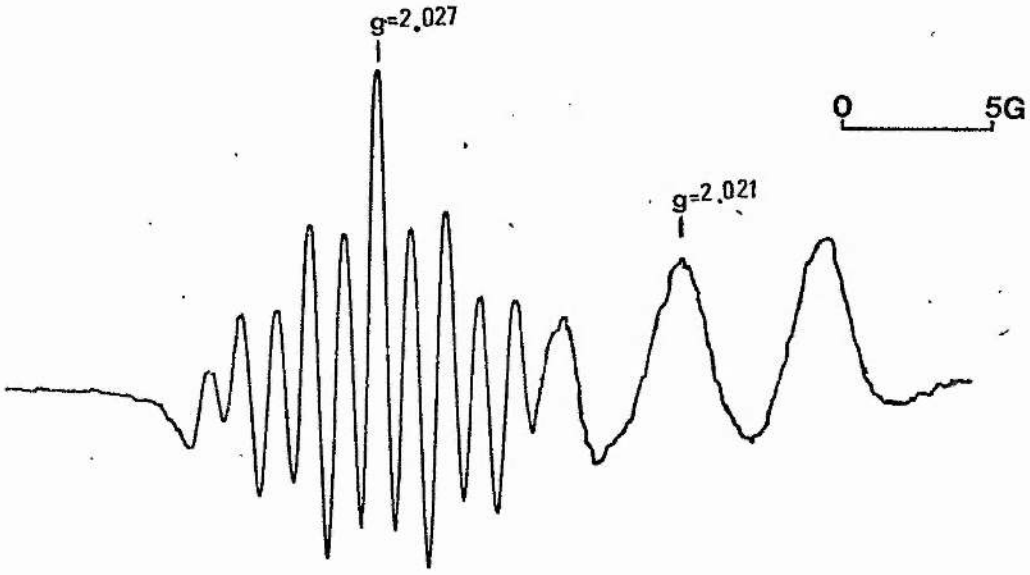


Fig. 6.2; E.p.r. spectrum of $[Fe(^{14}NO)_2(SPr^i)_2]^-$ and $[Fe(^{14}NO)(SPr^i)_3]^-$.

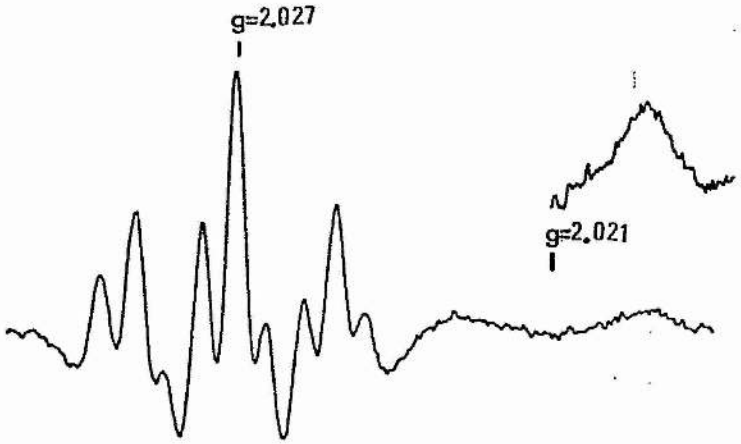


Fig. 6.3; E.p.r. spectrum of $[Fe(^{15}NO)_2(SPr^i)_2]^-$ and $[Fe(^{15}NO)(SPr^i)_3]^-$.

reliable assignment. Addition of sodium hydroxide to solutions of $[Fe_4S_3(NO)_7]^-$ in DMF caused no detectable change in the recorded e.p.r. spectrum. This disparity between water and DMF may perhaps be explained by the low solubility of the base in DMF.

In chapter 4 it was demonstrated that addition of RSNa to DMF solutions of $Fe_2(SR)_2(NO)_4$ caused the generation of strong e.p.r. spectra containing the mono-iron complex $[Fe(NO)_2(SR)_2]^-$. Repeating this study substituting $[Fe_4S_3(NO)_7]^-$ as the iron-nitrosyl substrate caused the production of a series of intense e.p.r. spectra. The resulting solutions contained two complexes, the first being the di-nitrosyl $[Fe(NO)_2(SR)_2]^-$, identified by comparison with spectra generated from $Fe_2(SR)_2(NO)_4$ and the second a mono-nitrosyl complex (table 6.1, fig. 6.2).

Table 6.1: E.p.r. data for $[Fe(^{14}NO)_2(SR)_2]^-$ and $[Fe(^{14}NO)(SR)_3]^-$ generated from $[Fe_4S_3(^{14}NO)_7]^-$.

	$[Fe(NO)_2(SR)_2]^-$			$[Fe(NO)(SR)_3]^-$	
R	g	$A(^{14}N)$/G	$A(^{1}H)$/G	g	$A(^{14}N)$/G
H	2.028	2.7	0.5	2.020	5.0
Me	2.028	2.1	2.1	2.021	4.5
Et	2.027	2.0	2.6	2.021	4.6
Pr^i	2.027	2.5	1.3	2.021	5.0
Bu^t	2.027	2.7	-	2.021	5.0
$PhCH_2$	2.027	2.4	1.4	2.021	4.8

The mono-nitrosyl complexes thus produced are similar to that produced

by the action of base on aqueous solutions in that the only resolved hyperfine coupling was that between the paramagnetic centre and the single nitrosyl ligand. Although no resolution of any hyperfine coupling to any α-protons of ligated RS^- was achieved, it can be assumed that RS^- is ligated, since the magnitude of the coupling varied with the degree at substitution of the α-carbon. This is as with $[Fe(NO)_2(SR)_2]^-$ (cf. chapter 4) where the magnitude of the nitrogen's hyperfine coupling is likewise directly proportional to the degree of substitution of the added thiolate. The observation of a variation of A(N) with R, and the assumption of four-coordinate iron, as in $[Fe(NO)_2(SR)_2]^-$ lead then to a tentative assignment of the constitution $[Fe(SR)_3(NO)]^{-x}$ to these species: if these species were formed from the apical iron of $[Fe_4S_3(NO)_7]^-$ without change of oxidation state, then x=1. It was found that addition of $R'S^-$ to DMF solutions containing $[Fe(NO)(SR)_3]^-$ caused a change in the magnitude of A(N) to that appropriate for $[Fe(NO)(SR')_3]^-$, which had been generated from the action of $R'S^-$ on $[Fe_4S_3(NO)_7]^-$. This demonstrates that, as in $[Fe(NO)_2(SR)_2]^-$, the alkane thiolato ligands in $[Fe(NO)(SR)_3]^-$ are labile to exchange. The absence of any resolved hyperfine coupling to hydrogen in the SR groups may be the result of a small A(H) value combined with a large line width (ca. 2.5G), or the consequence of fast ligand exchange.

The isotopes ^{15}N and ^{14}N differ both in their spin (I=1/2 vs I=1) and also in the magnitude of their A^o_{iso} values (29%)[19]. The ^{15}N analogue of $[Fe_4S_3(NO)_7]^-$ was treated with RS^- in DMF to confirm the spectral assignments above and also those reported in chapter 4 for the complex $[Fe(NO)_2(SR)_2]^-$ generated from $Fe_2(SR)_2(NO)_4$ (table 6.2,

fig. 6.3).

Table 6.2: E.p.r. data for $[Fe(^{15}NO)_2(SR)_2]^-$ and $[Fe(^{15}NO)(SR)_3]^-$ generated from $[Fe_4S_3(^{15}NO)_7]^-$.

	$[Fe(NO)_2(SR)_2]^-$			$[Fe(NO)(SR)_3]^-$	
R	g	$A(^{15}N)$/G	$A(^1H)$/G	g	$A(^{15}N)$/G
H	2.028	3.6	0.5	2.020	6.9
Me	2.027	3.0	2.1	2.021	6.9
Et	2.027	3.6	2.0	2.021	6.7
Pr^i	2.027	3.6	1.3	2.021	7.0
Bu^t	2.027	3.8	-	2.021	7.0
$PhCH_2$	2.027	3.3	1.5	2.021	6.9

The ratio $A^{15}N/A^{14}N$ for each of these complexes agrees reasonably well with that of $A^o_{iso}\ ^{15}N/A^o_{iso}\ ^{14}N$ and thus confirms the assignments.

As with the observations of $Fe_2(SR)_2(NO)_4$ in DMF (cf. chapter 4) the spectral strength was dependent upon the concentration of the base RS^-. Spectral composition was found to be temperature dependent: for a typical mixture where R=Me the initial concentration ratio of $[Fe(SMe)_2(NO)_2]^-/[Fe(SMe)_3(NO)]^-$, measured immediately after addition of RS^-, was *ca.* 1:2 at 290K and *ca.* 4:1 at 240K. The temperature dependence of the ratio is confirmed by variable temperature examination of the mixtures, the relative ratios reversibly changing with temperature. The monoanion $[Fe_4S_3(NO)_7]^-$ is composed of a 3:1 ratio of $Fe(NO)_2/Fe(NO)$, hence if the compound were to be split up into mono-iron fragments then a 3:1 ratio of $Fe(NO)_2/Fe(NO)$ would be observed. In chapter 4 it is shown that

$[Fe(NO)_2(SR)_2]^-$ exists in an equilibrium with the dinuclear $Fe_2(SR)_2(NO)_4$ (equation 3).

$$2[Fe(NO)_2(SR)_2]^- \rightleftharpoons Fe_2(SR)_2(NO)_4 + 2RS^- \qquad (3)$$

At ambient spectrometer temperature the equilibrium favours the di-iron complex, but, as the temperature is lowered, the mono-iron complex becomes more favoured. This explains the temperature dependence of the spectra from the reaction of $[Fe_4S_3(NO)_7]^-$ with RS^-. The reaction of $[Fe_4S_3(NO)_7]^-$ with RS^- in DMF can be summarised,

$$[Fe_4S_3(NO)_7]^- \xrightarrow[DMF]{RS^-} [Fe(NO)(SR)_3]^{-x} + 3/2\{2[Fe(NO)_2(SR)_2]^- \rightleftharpoons Fe_2(SR)_2(NO)_4\}$$

$$[3Fe(-1)(basal),1Fe(+1)(apical)] \longrightarrow Fe(+1) + 3Fe(-1)$$

When R=Alkyl, the complex $[Fe(NO)_2(SR)_2]^-$ appears to be the precursor of $Fe_2(SR)_2(NO)_4$, since the reaction of MeS^- with $[Fe_4S_3(NO)_7]^-$ yielded $Fe_2(SMe)_2(NO)_4$ in a 46% purified, isolated yield. On the other hand, reaction of $PPN^+[Fe_4S_3(NO)_7]^-$ with NaSH yielded $(PPN^+)_2[Fe_2S_2(NO)_4]^{-2}$, the formation of which may be described, thus:

$$[Fe_4S_3(NO)_7]^- \xrightarrow{SH^-} [Fe(SH)_2(NO)_2]^- \longrightarrow Fe_2(SH)_2(NO)_4$$

$$\xrightarrow[-H_2S]{+SH^-} [Fe_2S_2(NO)_4]^{-2}$$

In general the anions $[Fe(SR)_2(NO)_2]^-$ lose one mole of RS^- to yield $Fe_2(SR)_2(NO)_4$: if R=alkyl, this is the product which is isolated, but

when R=H, deprotonation is effected by excess SH^-, followed by the precipitation of the salt $(PPN^+)[Fe_2S_2(NO)_4]^{-2}$. In support of this suggestion that the initially formed $Fe_2(SH)_2(NO)_4$ is deprotonated in the presence of excess SH^-, it should be noted that Beck[20] in his protonation of the anion $[Fe_2S_2(NO)_4]^{-2}$ required the use of acids as strong as trifluoroacetic acid or HBF_4.

Reaction of the sodium salt of $[Fe_4S_3(NO)_7]^-$, which crystallises from water as a monohydrate, with elemental sulphur in DMF, yielded an e.p.r. spectrum which indicated a mixture of $[Fe(SH)_2(NO)_2]^-$ and $Fe(NO)_2(SH)(SH_2)$, together with a trace of mono-nitrosyl $[Fe(SH_3)(NO)]^-$. The mono-nitrosyl species generated in all of these examinations disappeared with time, and in all cases had disappeared after two days leaving only the spectrum of $[Fe(NO)_2(SR)_2]^-$.

6.3.2 Nitrosyl Exchange Reactions: Interconversion of Fe(NO) and $Fe(NO)_2$; $Fe(NO)_2$ and $Fe(^*NO)_2$; and Fe(NO) and $Fe(^*NO)$.

DMF solutions of $[Fe_4S_3(NO)_7]^-$ react with RS^- in the presence of NO_2^- to yield spectra composed solely of di-nitrosyl iron fragments. Immediate examination of mixtures containing $[Fe_4S_3(^{15}NO)_7]^-$, $^{14}NO_2^-$ and RS^- yielded spectra composed of a 3:1 mixture of the two species $[Fe(^{15}NO)_2(SR)_2]^-$ and $[Fe(^{15}NO)(^{14}NO)(SR)_2]^-$. Likewise, immediate examination of mixtures containing $[Fe_4S_3(^{14}NO)_7]^-$, $^{15}NO_2^-$ and RS^- yielded spectra composed of a 3:1 mixture of the two species $[Fe(^{14}NO)_2(SR)_2]^-$ and $[Fe(^{14}NO)(^{15}NO)(SR)_2]^-$. This suggests that all of the mono-nitrosyl species have reacted with nitrite to yield

di-nitrosyl species.

$$[Fe_4S_3(NO)_7]^- \xrightarrow{RS^-} [Fe(NO)_2(SR)_2]^- + [Fe(NO)(SR)_3]^-$$

$$[Fe(NO)(SR)_3]^- \xrightarrow{{}^*NO_2^-} [Fe(NO)({}^*NO)(SR)_2]^-$$

Allowing these solutions to age in the presence of an excess of ${}^*NO_2^-$ a second slower process was observed, that of ${}^*NO$ exchange for NO.

$$[Fe(NO)_2(SR)_2]^- \xrightarrow{{}^*NO_2^-} [Fe(NO)({}^*NO)(SR)_2]^-$$

$$[Fe(NO)({}^*NO)(SR)_2]^- \xrightarrow{{}^*NO_2^-} [Fe({}^*NO)_2(SR)_2]^-$$

Repeating this examination, substituting $Fe_2(SR)_2(NO)_4$ for $[Fe_4S_3(NO)_7]^-$, resulted in the observation of a slow nitrosyl exchange process. Thus confirming that the initial production of the mixed nitrosyl from $[Fe_4S_3(NO)_7]^-$ was from the addition of a nitrosyl to the apical Fe-NO fragment, rather than from a fast exchange of 'NO' between the di-nitrosyl fragments and the nitrite.

Reaction of an equimolar mixture of $[Fe_4S_3({}^{14}NO)_7]^-$ and $[Fe_4S_3({}^{15}NO)_7]^-$ with RS^- in DMF resulted in the production of a mixture containing $[Fe({}^{15}NO)_2(SR)_2]^-$, $[Fe({}^{14}NO)_2(SR)_2]^-$, $[Fe({}^{15}NO)(SR)_3]^-$ and $[Fe({}^{14}NO)(SR)_3]^-$. On standing the concentration of $[Fe(NO)(SR)_3]^-$ decreased and a new species $[Fe({}^{15}NO)({}^{14}NO)(SR)_2]^-$ was detected in low concentrations. This suggests that the observed reduction in magnitude of the spectrum of the mono-nitrosyl fragment results from a disproportionation to yield the di-nitrosyl species.

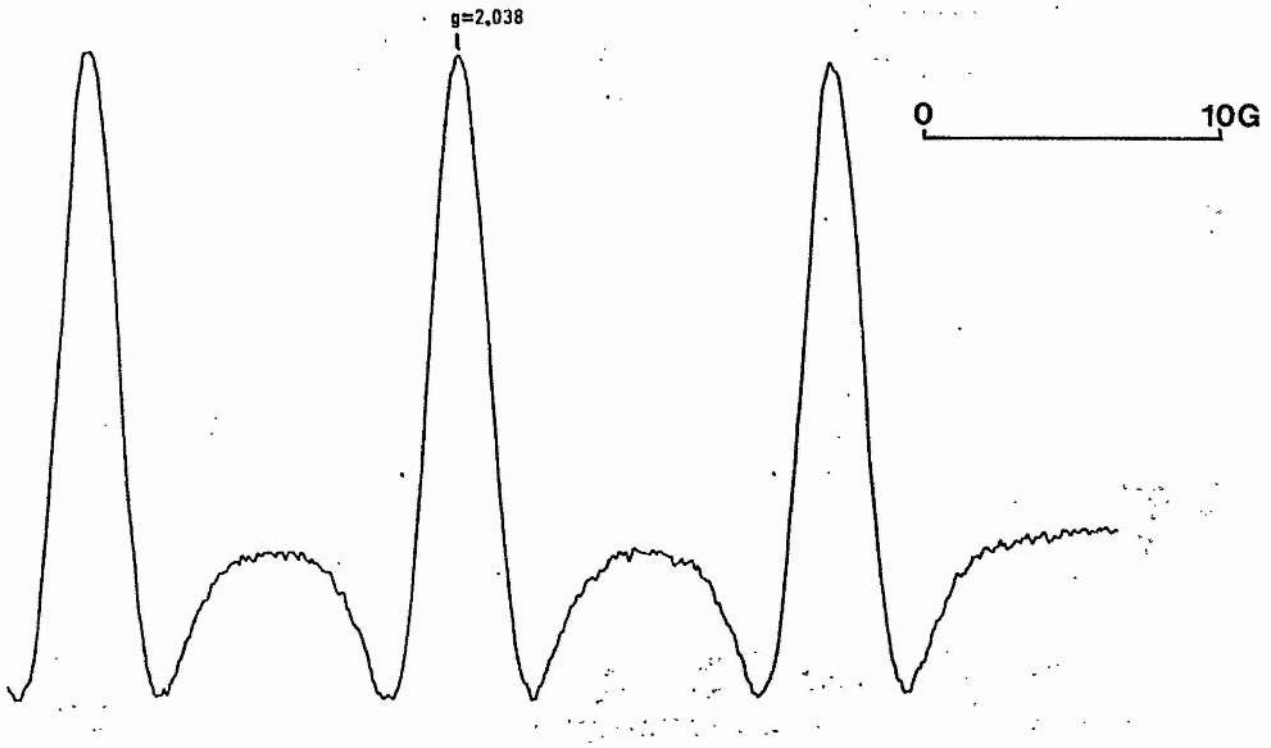


Fig. 6.4; E.p.r. spectrum of $Fe(^{14}NO)(S_2CNMe_2)_2$.

$$2[Fe(NO)_2]^{2+} \longrightarrow [Fe(NO)_2]^{+} + Fe^{+3}$$

$$2Fe(I) \longrightarrow Fe(-I) + Fe(III)$$

Attempts to isolate the mono-nitrosyl species $[Fe(NO)(SR)_3]^-$ proved unsuccessful. It has been shown that iron(II) salts react with nitrite and the dimethyldithiocarbamate ligand ($Me_2NCS_2^-$) to yield the relatively stable paramagnetic mono-iron species $Fe(NO)(S_2CNMe_2)_2$ (fig. 6.4)[15,21]. The iron in this complex has the same formal oxidation state as that of the mono-nitrosyl fragments in both $[Fe_4S_3(NO)_7]^-$ and in $Fe_4S_4(NO)_4$ of +1(d^7). $Fe(NO)(S_2CNMe_2)_2$ is hence a relatively good model of the mono-nitrosyl sites in these complexes. E.p.r. examination of authentic samples of this complex in either DMF or chloroform yielded a triplet (g=2.038, A(N)=13.2G), the only hyperfine coupling resolved being that due to the single nitrosyl ligand. Addition of $Me_2NCS_2^-$ to DMF solutions of $[Fe_4S_3(NO)_7]^-$, resulted in the generation of e.p.r. spectra identical to that obtained for authentic samples of $Fe(NO)(S_2CNMe_2)_2$. The e.p.r. spectra thus generated were found to contain no paramagnetic di-nitrosyl mono-iron fragments. Repeating this reaction on a preparative scale resulted in an isolation of the mono-nitrosyl complex in an 88% yield based upon total iron, i.e. not only the apical Fe(NO), but also the basal $Fe(NO)_2$ groups in $[Fe_4S_3(NO)_7]^-$ were converted to $Fe(NO)(S_2CNMe_2)_2$. The conversion of di-nitrosyls to mono-nitrosyls was found to be further demonstrated by the addition of $Me_2NCS_2^-$ to DMF solutions of either $Fe_2(SR)_2(NO)_4$ or $Fe_2I_2(NO)_4$. In

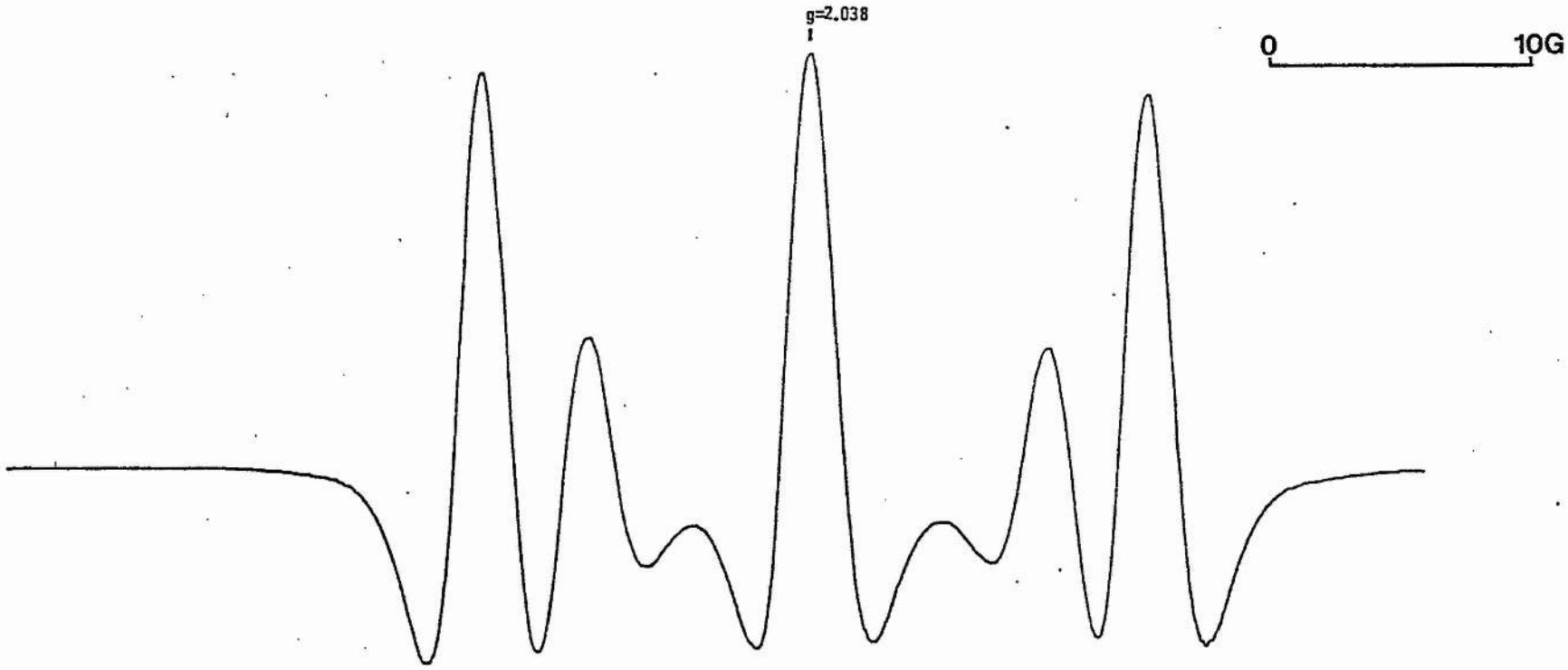
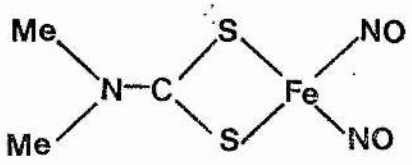
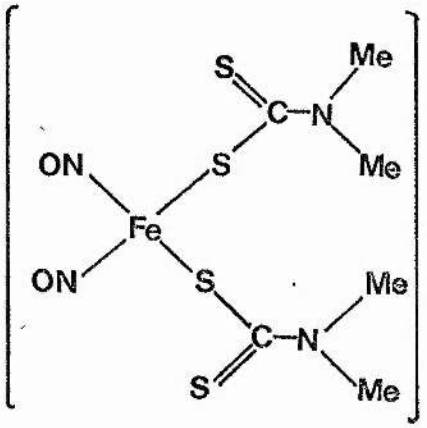


Fig. 6.5; E.p.r. spectrum of $Fe(^{14}NO)(S_2CNMe_2)_2$ and $Fe(^{15}NO)(S_2CNMe_2)_2$.

both cases the mono-nitrosyl $Fe(NO)(S_2CNMe_2)_2$ was immediately observed. In the reaction of $Fe_2(SR)_2(NO)_4$ with $Me_2NCS_2^-$ a weak quintet spectrum was detected which was observed to diminish with time ($g=2.030$, $A(N)=1.9G$). This spectrum can be assigned to either of



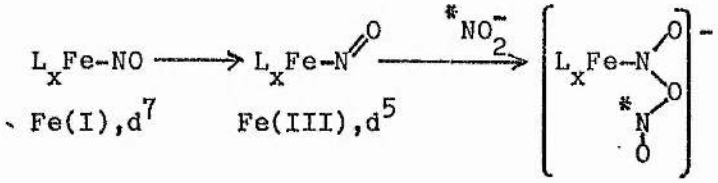
and

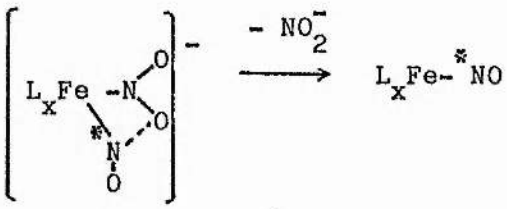


which are feasible intermediates in the conversion of the $Fe(NO)_2$ fragment in $Fe_2(SR)_2(NO)_4$ into the Fe(NO) fragment in $Fe(NO)(S_2CNMe_2)_2$. Repeating these reactions on a preparative scale yielded $Fe(NO)(S_2CNMe_2)_2$ from the iodo and alkane thiolato analogues in 35% and 41% isolated and purified yields. Thus $[Fe(NO)_2]^+$ and $[Fe(NO)]^{+2}$ are readily interconvertible.

Addition of NO_2^- to DMF solutions of $[Fe_4S_3(NO)_7]^-$ in the absence of air resulted in negligible change in the e.p.r. spectra. Addition of $Me_2NCS_2^-$ to DMF solutions of either $[Fe_4S_3(^{15}NO)_7]^-$ and $^{14}NO_2^-$, or $[Fe_4S_3(^{14}NO)_7]^-$ and $^{15}NO_2^-$, containing similar ratios of $^{14}N/^{15}N$, yielded essentially identical e.p.r. spectra, each characteristic of a mixture of $Fe(^{15}NO)(S_2CNMe_2)_2$ and $Fe(^{14}NO)(S_2CNMe_2)_2$ (fig. 6.5). Addition of a ten fold excess of $^{15}NO_2^-$ to $[Fe_4S_3(^{14}NO)_7]^-$ yielded essentially identical e.p.r. spectra when $Me_2NCS_2^-$ was added to the

mixture either immediately after addition of nitrite or after one month. This suggests that the rate of 'NO' exchange for mono-iron fragments is higher than that of any exchange which may occur on the tetra-iron cluster, $[Fe_4S_3(NO)_7]^-$. When $Fe(^{14}NO)(S_2CNMe_2)_2$ was treated in DMF solution with a large excess (>10:1 mol/mol) of $^{15}NO_2^-$, its e.p.r. spectrum was replaced, very rapidly and almost completely by that of $Fe(^{15}NO)(S_2CNMe_2)_2$, indicating fast exchange of the nitrosyl, possibly by a mechanism such as:





These results thus demonstrate that in addition to rapid exchange process demonstrated by the bridging chalcogen, halogen and pseudohalogen ligands (cf. chapters 4,5 and 6) the nitrosyl ligands in mono-iron fragments are labile to exchange.

6.3.3 Reactions of the cubane analogue $Fe_4S_4(NO)_4$.

As for the majority of metal cluster compounds, little of the chemistry of the cubane analogue $Fe_4S_4(NO)_4$ is known. The compound is composed of a tetrahedron of iron atoms, with a sulphur atom on each face and with a nitrosyl terminally bonded to each iron atom.[4]

Examination of this complex in non-polar solvents by ^{15}N n.m.r. spectroscopy reveals the compound to remain intact on dissolution. In DMF solution, $Fe_4S_4(NO)_4$ alone yielded a weak e.p.r. spectrum similar to that obtained for $[Fe_4S_3(NO)_7]^-$ and which indicated the presence of at least three paramagnetic centres. Addition of RS^- caused replacement of this spectrum with a new strong spectrum, the principle features of which were those due to $[Fe(NO)_2(SR)_2]^-$ together with those assigned earlier to $[Fe(NO)(SR)_3]^-$. This reaction can be summarised:

$$Fe_4S_4(NO)_4 \xrightarrow{12RS^-} 4[Fe(SR)_3(NO)]^- + 4S^{-2}$$

$$2[Fe(SR)_3NO]^- \longrightarrow [Fe(NO)_2(SR)_2]^- + [Fe(SR)_4]^-$$

$$2\ Fe(I) \longrightarrow Fe(-I) + Fe(III)$$

As with the corresponding reactions of $[Fe_4S_3(NO)_7]^-$, the e.p.r. spectrum of the mono-nitrosyl complex $[Fe(NO)(SR)_3]^-$ disappeared as the solution aged to leave only that of $[Fe(NO)_2(SR)_2]^-$.

However, when R=H, the observed behaviour is rather different: the initial spectrum consists of a mixture of $[Fe(NO)_2(SH)_2]^-$ and $[Fe(NO)(SH)_3]^-$, with g=2.020 and A(N)=5.0G. Examination of this mixture after one week showed the di-nitrosyl $[Fe(NO)_2(SH)_2]^-$ to be still present, whilst the mono-nitrosyl spectrum had been replaced completely by a new mono-nitrosyl spectrum with g=2.040 with only the nitrosyl coupling A(N)=13.5G resolved. Examination of this solution after another week found no trace of any paramagnetic mono-nitrosyl

fragments. A similar A(N)=13.5G mono-nitrosyl species were found to be observed with Bu^tS^-, where it was generated concurrently with $[Fe(NO)(SR)_3]^-$; and in the reaction of Pr^iSH with $Fe_2I_2(NO)_4$ in mixed THF/Et_3N solvent (cf. chapter 5). Although it proved impossible to isolate the mono-nitrosyl so as to fully characterise it, a plausible possibility for the constitution is $[Fe(NO)(SR)_3]^{-3}$, i.e. a d^9 iron complex, possibly formed by a disproportionation different from that defined above.

Repetition of the reaction of $Fe_4S_4(NO)_4$ with MeS^- on a preparative scale resulted in the isolation of $Fe_2(SMe)_2(NO)_4$ in an 13% overall yield, whilst the reaction of $Fe_4S_4(NO)_4$ with $Me_2NCS_2^-$ in DMF resulted in the isolation of $Fe(NO)(S_2CNMe_2)_2$ in almost quantitative (94%) purified yield. Comparison of the reactions of $Fe_2(SR)_2(NO)_4$, $Fe_4S_4(NO)_4$ and $[Fe_4S_3(NO)_7]^-$ shows that the nature of the principal paramagnetic product to be independent of the starting complex, but that it depends instead on the added ligand.

6.3.4 Reactions of $Fe(NO)(S_2CNMe_2)_2$ and attempts to generate $Fe(NO)(S_2P(OR)_2)_2$.

Addition of an excess of MeS^- to DMF solutions of $Fe(NO)(S_2CNMe_2)_2$ resulted in the observation of a slow conversion of the spectrum of the mono-nitrosyl to that of the di-nitrosyl $[Fe(NO)_2(SR)_2]^-$ with no other paramagnetic species detected. Repetition of this reaction on a preparative scale (in the presence of an excess of MeS^-) gave $Fe_2(SR)_2(NO)_4$ in a 24% isolated yield. Similarly $Fe(NO)(S_2CNMe_2)_2$ was

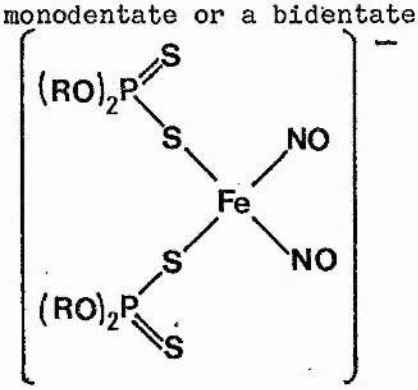
found to react with Na_2S in DMF to yield $[Fe_4S_3(NO)_7]^-$ in 18% isolated yield.

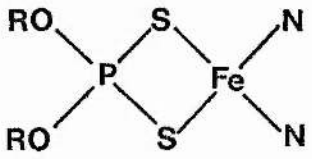
It appears that the nature of the observed paramagnetic species in all of these e.p.r. examinations in DMF is dependent upon the nature of any added ligands, in particular whether they are monodentate where di-nitrosyl complexes are the predominant species, or whether they are bidentate where mono-nitrosyls become the predominant species. In an attempt to explore the relationship between the nature of the thio-ligands and the stoichiometry of the resulting complexes the reactions of the dialkyl dithiophosphate $[(RO)_2PS_2^-]$ with a range of iron-nitrosyl substrates in DMF were studied. Like $Me_2NCS_2^-$ this ligand could, in principle, act as either a monodentate or as a bidentate chelating ligand: the S...S bite in chelating $(RO)_2PS_2^-$ is[22] ca. 3.28Å, whereas in $Me_2NCS_2^-$ [22,23] it is ca. 2.97Å. Attempts to isolate the $(RO)_2PS_2^-$ adduct of the mono-nitrosyl complex by a displacement reaction with $Fe(NO)(S_2CNMe_2)_2$ proved unsuccessful.

$$Fe(NO)(S_2CNMe_2)_2 + (RO)_2PS_2^- \longrightarrow\!\!\!\!\!\!\times\quad Fe(NO)(S_2P(OR_2)_2$$

Examination of DMF solutions containing both $Fe(NO)(S_2CNMe_2)_2$ and $(RO)_2PS_2^-$ were identical to those containing solely the mono-nitrosyl. However, addition of $(RO)_2PS_2^-$ to DMF solutions containing either $Fe_2I_2(NO)_4$ or $Fe_2(SR)_2(NO)_4$ resulted in the generation of intense e.p.r. spectra indicating the presence of both a di-nitrosyl (g=2.033, A(N)=2.3G) and a mono-nitrosyl complex (g=2.030, A(N)=2.2G). Essentially identical spectra were generated by the

action of $(RO)_2PS_2^-$ on DMF solutions of either $Fe_4S_4(NO)_4$ or $[Fe_4S_3(NO)_7]^-$. Spectral analysis was confirmed by the examination of $[Fe_4S_3(^{15}NO)_7]^-$ resulting in a relative decrease in the spectral multiplicity combined with a 40% increase in the hyperfine coupling. In none of these examinations was any hyperfine coupling to phosphorus (^{31}P,I=1/2) resolved. By analogy with $Fe(NO)(S_2CNMe_2)_2$ the mono-nitrosyl is assigned the constitution $Fe(NO)(S_2P(OR)_2)_2$ whilst the di-nitrosyl complex might have $(RO)_2P\ S_2^-$ bound in either a monodentate or a bidentate fashion.





All attempts to produce analytically pure samples of these complexes were unsuccessful, as the complexes were much less stable than that formed by the analogous $Me_2NCS_2^-$.

It can be concluded that the larger bite in the $(RO)_2PS_2^-$ does not result in the complex demonstrating any preference for the stabilisation of either mono or di-nitrosyl complexes in DMF solutions.

6.3.5 Reactions of $Fe(CO)_3(NO)^-$ salts.

In this section the results of an examination of the diamagnetic monoanion $[Fe(CO)_3(NO)]^-$ are reported. E.p.r. examination of DMF solutions of the salt $[Fe(CO)_3(NO)]^-(PPN)^+$ revealed it to be e.p.r. silent. Aged solutions were likewise e.p.r silent and it can be assumed that the compound is relatively stable in DMF and does not react to form paramagnetic solvo-complexes.

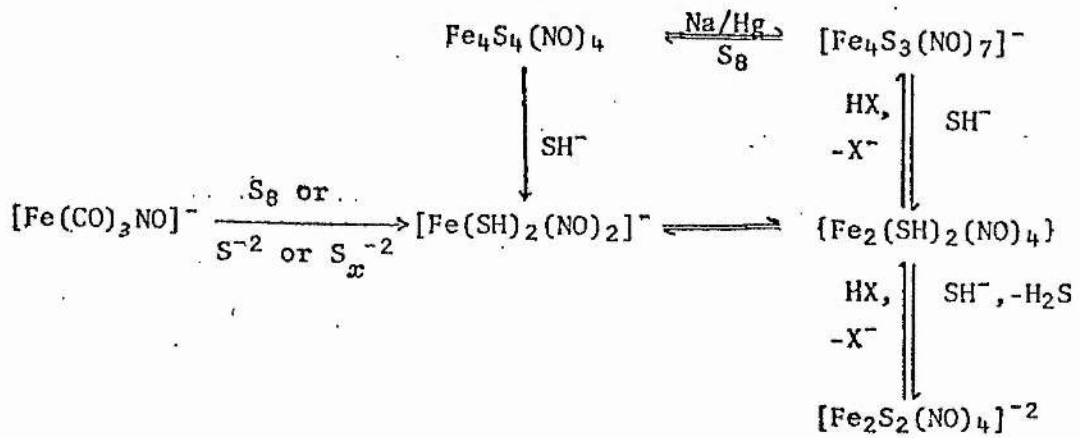
Upon addition of elemental sulphur, the solution readily gave a spectrum characteristic of $[Fe(SH)_2(NO)_2]^-$. Repeating this reaction on a preparative scale yielded the anion $[Fe_4S_3(NO)_7]^-$, the complex being formed immediately after mixing of the reactants; $(PPN)^+[Fe_4S_3(NO)_7]^-$ was subsequently isolated in an 84% yield. Prolonged reflux of the isolated salt in toluene with sulphur failed to yield $Fe_4S_4(NO)_4$. This is noteworthy since earlier work in this laboratory (cf. chapter 3) has shown that reflux of the sodium salt of $[Fe_4S_3(NO)_7]^-$ with elemental sulphur in toluene results in the formation of the cubane analogue in good yields. Likewise it has been shown that that the mercurial complex $Hg[Fe(CO)_3(NO)]_2^4$ reacts with sulphur to yield $Fe_4S_4(NO)_4$ as the sole isolable product. It is also known that the reaction of $Hg[Fe(CO)_3(NO)]_2$ with sodium polysulphide in methanol[24] results in the isolation of $Na[Fe_4S_3(NO)_7]$ rather than $Fe_4S_4(NO)_4$. Likewise refluxing the sodium salt with sulphur in a 100:1 toluene/acetone mixture, rendering the salt soluble, failed to yield $Fe_4S_4(NO)_4$, and the sole complex isolated, even after prolonged reflux, was $[Fe_4S_3(NO)_7]^-$. It is clear therefore that the formation

of $Fe_4S_4(NO)_4$ versus that of $[Fe_4S_3(NO)_7]^-$ is subject to subtle factors involving the solvent and the solubilities of both the reactants and the products.

The observation of $[Fe(NO)_2(SH)_2]^-$ in the reaction mixture of $[Fe(CO)_3(NO)]^-$ and sulphur, which yields ultimately $[Fe_4S_3(NO)_7]^-$, suggests that just as the reaction of $[Fe_4S_3(NO)_7]^-$ with OH^- or SH^- proceeds via $[Fe(NO)_2(SH)_2]^-$ on its way to $[Fe_2S_2(NO)_4]^{-2}$, so the formation of $[Fe_4S_3(NO)_7]^-$ proceeds via the same complex. This view is strengthened by the observation of $[Fe(NO)_2(SH)_2]^-$ in the reaction of $[Fe(CO)_3(NO)]^-$ with Na_2S, known[24] also to yield $[Fe_4S_3(NO)_7]^-$. Since preparative studies[16,20,25] have shown that $[Fe_2S_2(NO)_4]^{-2}$ and $[Fe_4S_3(NO)_7]^-$ are interconvertible:

$$[Fe_2S_2(NO)_4]^{-2} \rightleftharpoons [Fe_4S_3(NO)_7]^-$$

the fate of the $[Fe(NO)_2(SH)_2]^-$ will in general depend on the nature of the reaction medium. The relationship between all the complexes which are[1,16,20,24,25] interconnected via $[Fe(NO)_2(SH)_2]^-$ are summarised in scheme 2.



Just as S^{-2}/HS^- react with $[Fe(CO)_3(NO)]^-$ to yield $[Fe(NO)_2(SH)_2]^-$, the reaction of RS^- yields $[Fe(NO)_2(SR)_2]^-$. Preparative scale reaction of $[Fe(CO)_3(NO)]^-$ with an excess of MeS^- resulted in the isolation of $Fe_2(SMe)_2(NO)_4$ in 78% isolated, purified yield.

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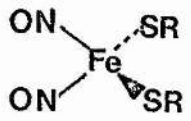
CHAPTER SEVEN

REACTIONS OF IRON-SULPHUR CLUSTERS WITH NITROSYLATING AGENTS.

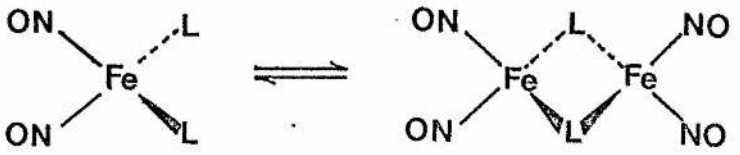
7.1 Introduction

In a study of the livers of rats treated with carcinogens[1], e.p.r. spectra have been obtained, which have been assigned to an iron-nitrosyl complex coordinated to a thiol containing protein:



Similar spectra have been recorded for various animal tissues incubated in nitrate[2], nitrite[2,3], hydroxylamine[2], and N-nitrosamines[2,4]. The spectra are weak and possess no resolvable hyperfine coupling to the paramagnetic centre, the assignment being based solely on the g-centre. It has been suggested that these complexes are generated by the action of the nitrosylating agents on the naturally occurring non-heme iron-sulphur proteins . However, to date, no report has been made on attempts to nitrosylate *in vitro* either isolated iron-sulphur proteins or their analogous synthetic models.

In chapters 4 and 5, it is shown that the mono-iron species $Fe(NO)_2L_2$ (L=halogen, alkylthiolate) exist in a dynamic equilibrium with the diamagnetic dinuclear analogues.



The methyl ester of Roussin's Red salt, $Fe_2(SMe)_2(NO)_4$, has been isolated from 'pickled' vegetables[5] and it has been suggested that this compound and its mononuclear analogues are derived from the naturally occurring iron-sulphur clusters contained in these vegetables.

In this chapter the results of a preliminary study on the nitrosylation of synthetic models of the naturally occurring iron-sulphur proteins are reported. The methods applied are those developed and reported in chapters 2,4,5 and 6.

If these iron-nitrosyl complexes are involved in chemical carcinogenesis then several questions arise. What is their action? Is it the disruption of the biochemical processes of the iron-sulphur cluster which induces carcinogenesis? Are these complexes 'intermediates' which release 'NO' ('NO' being the range of species: $NO^{\bullet}$, NO^{+}, H_2ONO^{+}, etc.) to effect some other biochemical process?

Molecular orbital calculations have been performed on several different iron-sulphur nitrosyl complexes[6,7]; the results suggest that both addition or removal of electrons weaken the clusters but do not cause direct ejection of nitric oxide. This agrees with experimental observations of Dahl and coworkers[6,8] who have shown by cyclic voltametry that several of these complexes can have variable oxidation states and that, as these complexes are successively reduced, they become less stable. The results of the reactions of $Fe_2(SR)_2(NO)_4$ and $[Fe_4S_3(NO)_7]^-$ with weak oxidising agents are recorded and discussed.

7.2 Experimental

7.2.1 Instruments and Materials.

Samples of $[Fe_2S_2((SCH_2)_2C_6H_4)_2]^{-2}$ [9] and $[Fe_4S_4(SCH_2Ph)_4]^{-2}$ [10] were prepared by literature methods. Samples of $Fe_2(SR)_2(NO)_4$ were prepared as described in chapter 2 and 4. $[Fe_4S_3(NO)_7]^-$ was prepared as described in chapter 6. All manipulations were carried out in an atmosphere of dry nitrogen: all organic solvents were purified, dried, and purged with dry nitrogen before use. All chemicals employed were A.R. or the purest commercially available.

E.p.r. spectra were measured at 240K, in 1 mm quartz capillaries using a Bruker 200D spectrometer. Di-t-butyl nitroxide was employed as the standard for the measurement of line positions. N.m.r. spectra were measured at ambient spectrometer temperature (308K) using a Bruker WP-80 machine. I.r. spectra were recorded on a Perkin-Elmer spectrometer as chloroform solutions. Mass spectra were recorded on an AEI MS 902 machine.

7.2.2 Reaction of 2Fe-2S and 4Fe-4S complexes with nitrite and nitric oxide.

(a)Reaction with alkaline/acidic nitrite. $[Fe_2S_2((SCH_2)_2C_6H_4)_2]^{-2}$ and $[Fe_4S_4(SCH_2Ph)_4]^{-2}$ were reacted with alkaline/acidic nitrite as described in chapter 2 to yield $[Fe_4S_3(NO)_7]^-$ in 44% and 38% yields respectively.

(b)Reaction with nitric oxide. $[Fe_2S_2(SCH_2Ph)_4]^{-2}$ (0.10g) was dissolved in $CHCl_3$ (30 ml) under nitrogen and nitric oxide bubbled through the mixture, this resulted in a change in colour from blue to red. Continued bubbling with reflux resulted in a second slower reaction, yielding an orange-red solution. The $CHCl_3$ solution was allowed to cool before washing with water (2 x 50 ml), filtering and drying over $MgSO_4$. The organic extract was reduced to solid and o-xylene-α,α'-disulphide ($C_6H_4(CH_2S)_2$) sublimed out of the mixture on the vacuum system (analysis: mass spec. m/z 168 (molecular ion), ^1H n.m.r. 7.2 and 3.8 p.p.m., absence of acid protons in both n.m.r.

and i.r. spectra). The components remaining in the the red solid were separated by dry column chromatography (100 cm x 1.5 cm; Silica Woelm) eluting with hexane (100 ml), followed by 50 ml aliquots hexane/CH_2Cl_2 mixtures (9:1, 3:1, 1:1, 1:3, and 1:9) followed by methylene chloride (100 ml) and 1:1 CH_2Cl_2/MeOH (100 ml). This yielded three red iron-nitrosyl bands which were examined by i.r., e.p.r., and n.m.r. spectroscopy. All three iron-nitrosyls gave absorptions at 1810(w), 1775(s), 1750(m)cm^{-1} in their i.r. spectra, identical to that for $Fe_2(SR)_2(NO)_4$. Compound one possessed i.r. absorptions similar to those of $[C_6H_4(CH_2S)_2]^{-2}$. Compound three contained i.r. absorptions similar to those of $[Et_4N]^+$ and compound two a mixture of both. The ^1H n.m.r. spectrum of compound one possessed n.m.r. resonances similar to that of $[C_6H_4(CH_2S)_2]^{-2}$ (7.2 and 3.8 p.p.m.). Compound three possessed n.m.r. resonances similar to that of $[Et_4N]^+$ (3.4 and 1.4 p.p.m.), whilst compound two appeared to contain a mixture of both.

7.2.3 E.p.r. examination of the reactions of solutions of 2Fe-2S and 4Fe-4S clusters with various nitrosylating agents.

In a typical reaction the iron sulphur complex was dissolved in DMF (previously deoxygenated by bubbling dry nitrogen). To this solution was added the reactant and the e.p.r. spectrum recorded at 240K.

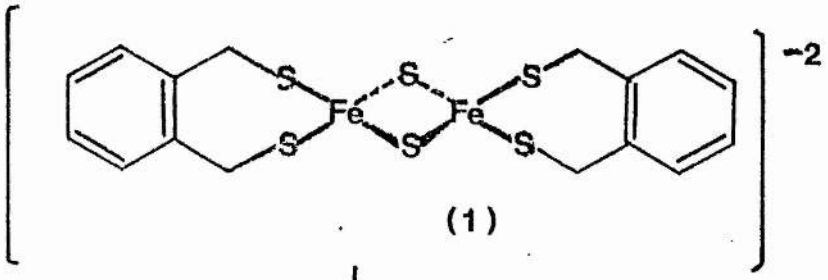
7.2.4 Reaction of $[Fe_4S_3(NO)_7]^-$ with weak oxidising agents.

(a) With Ag(I) and Cu(II). Addition of either aqueous solutions of $AgNO_3$ or $CuSO_4$ to $[Fe_4S_3(NO)_7]^-$ resulted in the evolution of nitric oxide (detected by mass spectroscopy) and precipitation of copper sulphide or silver sulphide together with sulphur.

(b) With I_3^- and Br_3^-. (i) Addition of aqueous solutions of either I_3^- or Br_3^- to solutions containing $[Fe_4S_3(NO)_7]^-$ resulted in the evolution of nitric oxide (detected by mass spectroscopy), precipitation of iron sulphide and elemental sulphur. Examination of the reaction of I_3^- with $[Fe_4S_3(NO)_7]^-$ by potentiometric titration yielded a sigmoid curve with end point equivalent to a 1.88:1 ratio. The reaction with Br_3^- was not as simple, a secondary reaction between the precipitated sulphur and Br_3^- being observed.

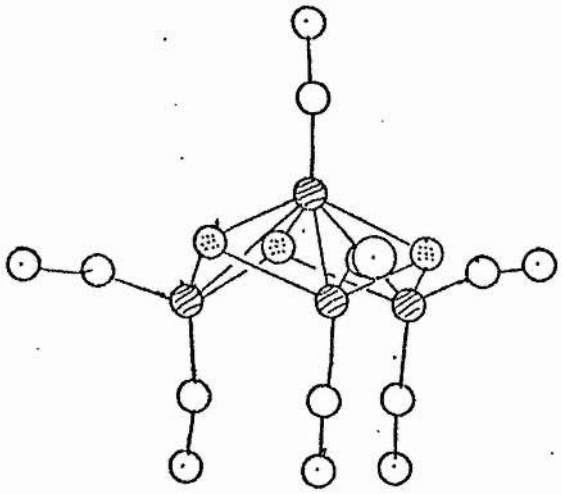
7.2.5 Reaction of $[Fe_4S_3(NO)_7]^-$ and $Fe_2(SEt)_2(NO)_4$ with N-methyl aniline.

Reflux of either $[Fe_4S_3(NO)_7]^-$ or $Fe_2(SEt)_2(NO)_4$ in $HClO_4$ (10^{-2}M) resulted in the complete decomposition of the complexes. Addition of N-methyl aniline to these mixtures resulted in the production of N-nitroso methyl aniline (detected by u.v. spectroscopy (λ_{max} 275 nm) and GC/MS (m/z 136 (molecular ion)).



(1)

NO_2^-



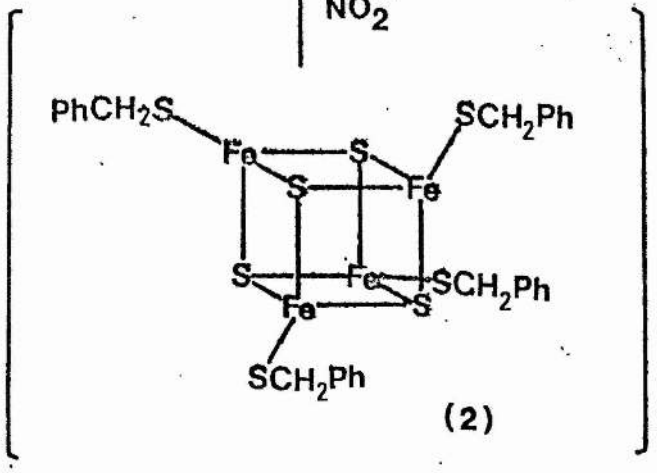
Fe

S

N

O

NO_2^-



(2)

Conversion of iron-sulphur protein models into $[Fe_4S_3(NO)_7]^-$

7.3 Results and Discussion

7.3.1 Nitrosylation of iron-sulphur complexes.

Nitrosylation of the tetraethylammonium salt of the di-iron sulphur complex bis[o-xylene- α , α' -dithiolato-μ_2-sulphido-ferrate(III)]$^{-2}$ (1) ($[Fe_2S_2((SCH_2)_2C_6H_4)_2]^{-2}$) by the application of aqueous alkaline nitrite followed by addition of acid as described in chapter 2 yielded the non isostructural iron-nitrosyl $[Fe_4S_3(NO)_7]^-$. The isolation of $[Fe_4S_3(NO)_7]^-$ rather than $[Fe_2S_2(NO)_4]^{-2}$ is not particularly surprising since although the S-alkylated iron carbonyl: $Fe_2(SR)_2(CO)_6$ yields its nitrosyl analogue $Fe_2(SMe)_2(NO)_4$ by this method, and the non alkylated bridging sulphur complexes $Fe_3S_2(CO)_9$, $Fe_2S_2(CO)_6$, and $[Fe_2S_2(CO)_6]^{-2}$ all yield $[Fe_4S_3(NO)_7]^-$ (cf. chapter 2). It has been previously shown[11-13] that $[Fe_4S_3(NO)_7]^-$ and $[Fe_2S_2(NO)_4]^{-2}$ exist in a pH-dependent equilibrium

$$[Fe_4S_3(NO)_7]^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [Fe_2S_2(NO)_4]^{-2}$$

with $[Fe_4S_3(NO)_7]^-$ predominant in acid. It is unsurprising, therefore, that $[Fe_4S_3(NO)_7]^-$ rather than $[Fe_2S_2(NO)_4]^{-2}$ is isolated from these nitrosylation reactions since the final step of reaction requires acidification. In the nitrosylation of $[Fe_2S_2((SCH_2)_2C_6H_4)_2]^{-2}$, $[Fe_4S_3(NO)_7]^-$ was isolated in a 44% yield based on iron, the rest of the iron being isolated as iron sulphide.

The nitrosylation reaction using aqueous nitrite was repeated on the 4Fe-4S model $[Fe_4(\mu_3\text{-}S)_4(SCH_2Ph)_4]^{-2}$ (2) resulting in the isolation of $[Fe_4S_3(NO)_7]^-$ in a 38% yield.

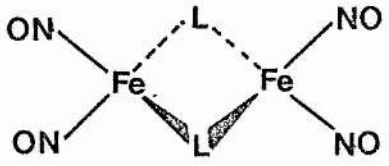
The interconvertibility of $[Fe_4S_3(NO)_7]^-$ and $Fe_2(SR)_2(NO)_4$ is demonstrated in chapter 6, and hence the 2Fe-2S cluster, $[Fe_2S_2((SCH_2)_2C_6H_4)_2]^{-2}$ and the 4Fe-4S cluster $[Fe_4S_4(SCH_2Ph)_4]^{-2}$ can be converted, at least in the laboratory, into $Fe_2(SMe)_2(NO)_4$. These two reactions thus demonstrate that the conversion of 4Fe-4S and 2Fe-2S clusters into $Fe_2(SMe)_2(NO)_4$, as isolated by Wang and coworkers[14] from pickled cabbage, is feasible.

In chapter 2 a second carbonyl/nitrosyl conversion reaction is described involving the application of nitric oxide:

$$Fe_2(SR)_2(CO)_6 \xrightarrow[CHCl_3]{NO} Fe_2(SR)_2(NO)_4$$

This reaction was repeated substituting $[Fe_2S_2((SCH_2)_2C_6H_4)_2]^{-2}$ for the carbonyl substrate, and with continued NO bubbling a mixture of three chromatographically separable nitrosylated products were obtained. Examination of these three complexes by infra-red spectroscopy yielded identical nitrosyl absorptions to those observed for $Fe_2(SR)_2(NO)_4$.

Examination of these three complexes in chloroform yielded no detectable paramagnetic species by e.p.r. spectroscopy. However, substituting DMF for the solvent, weak unresolved spectra were obtained similar to that generated from $Fe_2(SR)_2(NO)_4$ (cf. chapter 4). Addition of Pr^iS^- to these DMF solutions yielded identical e.p.r. spectra to those assigned to $[Fe(NO)_2(SPr^i)_2]^-$ in chapter 4. These results suggest that the three compounds generated by the action of NO on $[Fe_2S_2((SCH_2)_2C_6H_4)_2]^{-2}$ in chloroform are 2Fe-4NO complexes similar to $Fe_2(SR)_2(NO)_4$. In chloroform the iron-sulphur ring remains intact, whilst in DMF ring opening occurs to yield paramagnetic mononuclear species. Each of the three complexes can be assumed to be of general structure:



The three iron-nitrosyl complexes isolated demonstrated different ^1H n.m.r. and i.r. spectra. The spectra of the first compound isolated by chromatography (see experimental) demonstrated the presence of o-xylene-α, α'-dithiolate but no Et_4N^+. The second demonstrated a mixture of the the thiolate and Et_4N^+ and the third Et_4N^+ and no thiolate. Insufficient material prevented complete elucidation of the structure of the isolated compounds, and this problem requires further investigation. During this examination

several other products were observed although not fully isolated due to the tiny quantities. In particular, four non-nitrosyl containing complexes (determined by the absence of any peaks in the i.r. spectra assignable to ν(NO)) were identified in the chromatographic isolation of the three nitrosyl products. Due to the lack of material it was not possible to determine whether each of the non-nitrosyl complexes were intermediates to the formation of the iron-nitrosyls or were only byproducts; or whether the iron-nitrosyls themselves were interconvertible. These points also require further work.

Nitric oxide is a good, clean oxidising agent for the conversion of thiols to disulphides[15]. In this reaction, in addition to converting the iron sulphur core to iron-nitrosyls, the nitric oxide also oxidised some of the dithiolate present to its disulphide (o-xylene-α,α'-disulphide).

7.3.2 Production of 2.03 complexes from iron-sulphur protein models by the action of various nitrosylating agents.

The action of various nitrosylating agents on mammalian cell cultures[2-4] has been found to generate paramagnetic species, observed as a series of weak, unresolved e.p.r. spectra. These complexes possess g-centres ca. 2.03 which have been assigned[1] to $[Fe(NO)_2]^+$

complexed to thiol containing proteins (fig. 7.1). In this section the results of an e.p.r. study of the reactions of solutions of $[Fe_2S_2((SCH_2)_2C_6H_4)_2]^{-2}$ and $[Fe_4S_4(SCH_2Ph)_4]^{-2}$ with a series of nitrosylating agents are reported. DMF was employed as a solvent throughout, since it is demonstrated in chapter 4 to be a good ring opening solvent for $Fe_2X_2(NO)_4$.

DMF solutions of the diamagnetic $[Fe_2((SCH_2)_2C_6H_4)_2]^{-2}$ react with nitric oxide to yield solutions containing an equimolar mixture of two paramagnetic species. These are similar to those observed in the solvolysis of $Fe_2(SR)_2(NO)_4$ in DMF (cf. chapter 4) and can be assigned to a mixture of $[Fe(NO)_2(Solv.)]^+$ and $Fe(NO)_2(SR)(Solv.)$ ($g=2.033$, $A(^{14}N)=2.4G(2N)$, $A(Solv.^1H)=4.0G(2H)$; $g=2.027$, $A(^{14}N)=2.5G(2N)$, $A(Solv.^1H)=4.4G(1H)$, $A(Thiol\ ^1H)=4.5G(2H)$). Addition of an excess of potassium iodide to this mixture converted the weak spectrum of $Fe(NO)_2(Solv)(SR)$ and $[Fe(NO)_2(Solv)_2]^+$ to a strong eleven line species identifiable as $[Fe(NO)_2I_2]^-$ (cf. chapter 5). Similarly, addition of Pr^iS^- yielded the characteristic spectra of $[Fe(NO)_2(SPr^i)_2]^-$.

$$[Fe_2S_2((SCH_2)_2C_6H_4)_2]^{-2} \xrightarrow[DMF]{NO} [Fe(NO)_2(Solv.)_2]^+ + Fe(NO)_2(Solv.)(SR)$$

$$\xrightarrow{X^-} [Fe(NO)_2X_2]^-$$

Repeating this reaction, substituting $[Fe_4S_4(SCH_2Ph)_4]^{-2}$ as the solute yielded no detectable paramagnetic species by the action of nitric oxide at room temperature. However, combined refluxing with bubbling nitric oxide resulted in a solution containing at least two

paramagnetic species. Addition of iodide to this mixture yielded an eleven line species assignable to $[Fe(NO)_2I_2]^-$.

Addition of either $PPN[NO_2]$ or $NaNO_2$ to DMF solutions of $[Fe_2S_2((SCH_2)_2C_6H_4)_2)]^{-2}$ yielded a three line spectrum (g=2.031, $A(^{14}N)$=12.3g) assigned to a single nitrosyl coupled to iron(d^9). This species was found to be quickly replaced by a di-nitrosyl complex identical to that assigned in chapter 4 to $Fe(NO)_2(SH)(SH_2)$. Repeating this reaction substituting $[Fe_4S_4(SCH_2Ph)_4]^{-2}$ for $[Fe_2S_2((SCH_2)_2C_6H_4)_2)]^{-2}$ yielded a triplet spectrum assignable to a single nitrosyl coupled to iron(d^9). As above, this mono-nitrosyl complex was found to be quickly replaced by a di-nitrosyl complex, but in this case the spectrum obtained was identical to that generated by the addition of $NaNO_2$ to $Fe_2(SCH_2Ph)_2(NO)_4$ in DMF. Addition of KI to the complexes generated from $[Fe_2S_2((SCH_2)_2C_6H_4)_2]^{-2}$ and $[Fe_4S_4(SCH_2Ph)_4]]^{-2}$ both yielded the eleven line spectrum of $[Fe(NO)_2I_2]^-$.

Addition of the N-nitrosamine Me_2NNO to a DMF solution of $[Fe_2S_2((SCH_2)_2C_6H_4)_2]^{-2}$ yielded over a four day period no detectable paramagnetic iron-nitrosyl complexes and subsequent addition of KI to this solution failed to yield the eleven line spectrum of $[Fe(NO)_2I_2]^-$.

In conclusion, both NO and NO_2^- convert Fe_2S_2 and Fe_4S_4 complexes into both diamagnetic and paramagnetic iron-nitrosyl complexes. The action of both of these nitrosylating agents yields di-nitrosylated species and in the case of NO_2^- a mono-nitrosyl intermediate was

observed. The di-nitrosyl complexes in the presence of alkylthiolato ligands yield $[Fe(NO)_2(SR)_2]^-$ complexes identical to those reported in chapter 4. As observed in chapter 4 the alkylthiolato groups ligated to $[Fe(NO)_2]^+$ are labile to exchange, addition of halide ions or other alkylthiolates resulting in fast ligand exchange to yield paramagnetic species identical to those reported in chapters 4 and 5.

No paramagnetic iron-nitrosyl complexes were detected from the action of the N-nitrosamine Me_2NNO on $[Fe_2S_2((SCH_2)_2C_6H_4)_2]^{-2}$ in DMF. In chapter 5, it is recorded that the addition of iodide to the diamagnetic iron-nitrosyl complexes: $Fe_2I_2(NO)_4$ or $Fe_2(SR)_2(NO)_4$, results in ring fission to yield $[Fe(NO)_2I_2]^-$. The failure to observe $[Fe(NO)_2I_2]^-$ after addition of iodide to the N-nitrosamine containing mixture suggests that in addition to the absence of any paramagnetic iron-nitrosyl species, that no diamagnetic nitrosylated complexes labile to conversion to paramagnetic mono-iron species were present generated by the action of the N-nitrosamine on the iron-sulphur protein model. This is inconsistent with observations made of cell cultures treated with N-nitrosamines where weak, poorly resolved anisotropic e.p.r. spectra have been ascribed to $[Fe(NO)_2]^+$ coordinated to thiol containing proteins[4]. It is possible that the Fe-S clusters are converted by an indirect route, since, in addition to the biochemical processes of the Fe-S clusters in cells many other reactions will be occurring. One of these reactions may release the 'NO' from the N-nitrosamine to react with the Fe-S protein.

7.3.3 Nitrosyl elimination reactions of Iron-Nitrosyls.

In section 7.3.1 the formation of iron-nitrosyl complexes from synthetic models of iron-sulphur proteins is reported. These iron-nitrosyls have been implicated in carcinogenesis: however, question arise over the actual mode of their activity. These complexes may act as 'resting states' which can subsequently release 'NO' to cause nitrosation of biochemically important sites containing such groups as amines or thiols. It is noted in previous chapters that in addition to the lability to exchange of alkylthiolate and halide ions coordinated to $[Fe(NO)_2]^+$, the nitrosyl ligands are labile to exchange. Addition of either $[Me_2NCS_2^-]$ or $[(RO)_2PS_2^-]$ to $[Fe(NO)_2L_2]^-$ results in the formation of complexes containing iron coordinated to a single nitrosyl. Conversion of Roussins Red Salt to Roussins Black salt involves the loss of 'NO' from one of the four di-nitrosylated iron atoms to form the apical Fe-NO.

$$2[Fe_2S_2(NO)_4]^{-2} \xrightarrow{H^+} [Fe_4S_3(NO)_7]^-$$

In each of these reactions an iron-nitrosyl complex is converted into a second complex with a resultant loss of 'NO'. In the presence of added thiol DMF solutions of $Fe(NO)(S_2CNMe_2)_2$ react to yield paramagnetic mono-iron di-nitrosyl complexes. This is found also with $Fe_4S_4(NO)_4$ ($\equiv[Fe(NO)S]_4$) and $[Fe(CO)_3(NO)]^-$ and since no additional 'NO' is added to these mixtures and the di-nitrosyl complexes generated must result from a 'NO' transfer. This can be summarised in the case of $Fe_4S_4(NO)_4$ and $Fe(NO)(S_2CNMe_2)_2$ as;

$$2[Fe^{I}(NO)]^{+2} \longrightarrow [Fe^{-I}(NO)_2]^+ + Fe^{III}$$

Hence, it is possible at least in the laboratory, to abstract 'NO' from iron-nitrosyl complexes, the resulting denitrosylated iron atoms if in a biological system would then be free for reincorporation into iron-sulphur proteins. In e.p.r. examinations of mammalian cells[1-4], treatment with nitrite resulted in the generation of '2.03' complexes. Examination of these cell cultures revealed that the species were relatively short lived. This is an important observation since it demonstrates that a reaction must have occurred, which may have returned the activity to the iron-sulphur cluster and have also released 'NO' into some other biochemical site in the cell.

Both $Fe_2(SCH_2COOH)_2(NO)_4$ and $[Fe_4S_3(NO)_7]^-$ in aqueous solution were found to be readily, and completely, decomposed by the action of the weak oxidising agents I_3^-, Br_3^-, Ag(I) and Cu(II) resulting in the evolution of nitric oxide in each case. Indeed throughout the examination of the properties of these iron-sulphur nitrosyls, in particular in the case of the mononuclear species, caution had to be demonstrated to ensure that the complexes were not oxidised by contact with atmospheric oxygen.

The mode of nitrosyl transfer between two [Fe-NO] fragments is currently unknown. This process is not solely restricted to transfer between other iron-nitrosyls: Wang and coworkers[16] have found that $Fe_2(SR)_2(NO)_4$ reacts with amines in aqueous acid to yield N-nitrosamines. Repetition of this study with either $Fe_2(SEt)_2(NO)_4$ or $[Fe_4S_3(NO)_7]^-$ with N-methyl aniline resulted in the complete decomposition of the iron sulphur complexes and the production of the N-nitrosamine N-nitroso methyl aniline.

7.4 References.

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APPENDIX 1

Publications.

The following list of publications contains the results of my research for the period 1981-84.

1. Ligand exchange process in some iron-sulphur-carbonyl and nitrosyl complexes. POLYHEDRON 2, 1045 (1983).

2. The reported ion $Fe_3S_2(NO)_5^-$: a re-investigation. POLYHEDRON 2, 1399 (1983).

3. Formation of Bis(u-methanethiolato)-μ_4-thioxotetrakis -(tri-carbonyliron) in the Reaction between Dodecacarbonyltriiron and Dimethyldisulphide. INORGANICA CHEMICA ACTA 87, L15 (1984).

4. Iron-sulphur-carbonyl and -nitrosyl complexes: a laboratory experiment. JOURNAL OF CHEMICAL EDUCATION, in press.

5. Reactions of bis-μ-iodo-bis(dinitrosyliron) with halide ions and with thiols: an electron paramagnetic resonance study. POLYHEDRON, in press.

6. Formation of paramagnetic mono-nuclear iron nitrosyl complexes from diamagnetic di- and tetra-nuclear iron-sulphur nitrosyls: characterisation by e.p.r. spectroscopy and study of thiolate and nitrosyl ligand exchange reactions. POLYHEDRON, submitted.

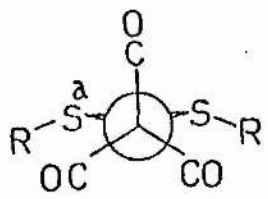
7. Variable-temperature and solvent n.m.r. study of bis(μ_2-methanethiolato)-bis(dinitrosyliron) and bis(μ_2-methane selenolato)-bis(dinitrosyliron). POLYHEDRON, submitted.

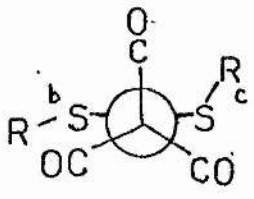
8. Homonuclear spin-spin coupling through iron in simple inorganic ions. POLYHEDRON, in press.

9. Nitrogen-15 and carbon-13 nuclear magnetic resonance study of Roussin salts and esters and some pentocyano iron complexes. INORGANIC CHEMISTRY, submitted.

10. Nitrosylation of 2Fe-2S and 4Fe-4S models for iron-sulphur redox proteins. POLYHEDRON, submitted.

Table 1: ^1H n.m.r. data for $Fe_2(SR)_2(CO)_6$





Conformation	a	b	c	
		Chemical Shift/p.p.m.		
R=CH_3				
$CDCl_3$	2.13	2.17	1.63	SCH_3
			1.17	
Toluene-d_8	1.50	1.57	1.17	SCH_3
R=Et				
$CDCl_3$	2.45	2.45	2.15	SCH_2
			1.85	
Toluene-d_8	2.07	2.07	1.85	SCH_2
$CDCl_3$	1.33	1.38	1.11	CH_3
Toluene-d_8	1.01	1.01	0.82	CH_3
R=Pr^i				
$CDCl_3$	d	d	d	SCH
			d	
Toluene-d_8	d	d	d	SCH
$CDCl_3$	1.35	1.39	1.16	CH_3
Toluene-d_8	1.03	1.09	0.91	CH_3
R=Pr^n				
$CDCl_3$	2.45	2.45	2.13	SCH_2
Toluene-d_8	2.08	2.08	1.89	SCH_2
$CDCl_3$	1.03	1.07	0.94	CH_3
Toluene-d_8	0.77	0.78	0.74	CH_3
R=Bu^n				
$CDCl_3$	2.47	2.47	2.15	SCH_2
Toluene-d_8	2.23	2.23	2.02	SCH_2
$CDCl_3$	0.95	0.95	0.90	CH_3
Toluene-d_8	0.81	0.81	0.72	CH_3

a.,b., and c. refer to their relevant conformations.

d. not resolved.

APPENDIX 2

^{1}H n.m.r. examination of $Fe_2(SR)_2(CO)_6$.

2.1 Experimental.

Alkyl analogues of $Fe_2(SR)_2(CO)_6$ were prepared by the literature method[1]. ^{1}H n.m.r. spectra were recorded for samples in both $CDCl_3$ and toluene-d_8 (table 1). ^{1}H n.m.r. spectra were recorded on a WP-80 Bruker machine.

2.2 Results.

As part of an investigation of the ASIS phenomena, the ^{1}H n.m.r. spectra were recorded for a series of alkanethiol derivatives of $Fe_2(SR)_2(CO)_6$ (R=Me,Et,Pr^i,Pr^n,Bu^n) in the $CDCl_3$ and toluene-d_8 solutions (Table 1).

$Fe_2(SR)_2(CO)_6$ can exist in three structural conformations[2], although for alkanethiol substituted analogues only two conformers have been identified[1]. Looking at the details of the ^{1}H chemical shifts listed in Table 1, it is notable that the shift in the resonances on changing solvents is in the same direction as that observed for $Fe_2(SR)_2(NO)_4$. The shift in resonance on changing solvent varies inversely with the distance of the protons from the iron-sulphur core. The magnitude of the shift is also affected by the length of the alkyl chain; the longer the chain the smaller the shift. Finally it is noted that the conformation of the alkyl chain

and the conformation of the chain adjacent to the observed chain affects the magnitude of the observed shift. These results agree with those observed for the solvent shift phenomena observed for $Fe_2(SR)_2(NO)_4$ (cf. chapter 3).

2.3 References.

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APPENDIX 3

^{13}C and ^{15}N n.m.r. examination of $[Fe(^{13}CN)_5(^{15}NO)]^{-2}$ and $[Fe(CN)_5(NO_2)]^{-4}$.

3.1 Experimental.

(a) Preparation of $[Fe(^{13}CN)_5(^{15}NO)]^{-2}$. To $[Fe(^{13}CN)_5(^{14}NO)]^{-2}$ (50 mg) prepared as described in literature[1] in D_2O (3 ml) was added $Na[^{15}NO_2]$ (50 mg), this mixture was stood in the dark under nitrogen for two weeks before examination by both ^{15}N and ^{13}C n.m.r..

(b) Preparation of $[Fe(^{13}CN)(^{15}NO_2)]^{-4}$. (i) To the solution prepared in (a), was added a small quantity of NaOH. The ^{15}N and ^{13}C n.m.r. spectra of this sample was recorded immediately after addition.
(ii) To $[Fe(^{13}CN)_5(^{14}NO)]^{-2}$ (50 mg) in D_2O (3 ml) was added a small quantity of NaOH. To this mixture was added $Na[^{15}NO_2]$ (50 mg) and the ^{15}N and ^{13}C n.m.r. spectra immediately recorded.

(c)Preparation of $[Fe(^{13}CN)_5(^{14}NO_2)]^{-4}$. To $[Fe(^{13}CN)_5(^{14}NO)]^{-2}$ (50 mg) in D_2O (3 ml) was added a small quantity of NaOH. The ^{13}C and ^{15}N n.m.r. of this mixture was recorded immediately after addition of the base, and after 15 hours.

^{15}N and ^{13}C n.m.r. spectra were recorded on the SERC Bruker WH-360 spectrometer at Edinburgh.

Table 1: ^{13}C and ^{15}N n.m.r. data for three isotopic forms of $[Fe(CN)_5(NO)]^{-2}$ and $[Fe(CN)_5NO_2]^{-4}$.

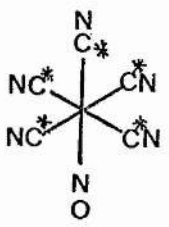
$[Fe(^{13}CN)_5(^{15}NO)]^{-2}$			
($^{13}C_{ax}$)	+132.4 p.p.m. (p x d)	$^2J(^{13}C_{ax}Fe^{13}C_{eq})$	17.7 Hz
($^{13}C_{eq}$)	+134.4 p.p.m. (d x d)	$^2J(^{13}C_{ax}Fe^{15}N)$	13.1 Hz
(^{15}N)	- 9.9 p.p.m. (d x p)	$^2J(^{13}C_{eq}Fe^{15}N)$	3.6 Hz
$[Fe(^{13}CN_{ax})(^{12}CN_{eq})(^{13}CN_{eq})_3(^{15}NO)]^{-2}$			
($^{13}C_{ax}$)	+132.4 p.p.m. (q x d)	$^2J(^{13}C_{ax}Fe^{13}C_{eq})$	17.6 Hz
($^{13}C_{eq}$)	b	$^2J(^{13}C_{ax}Fe^{15}N)$	13.1 Hz
(^{15}N)	- 9.9 p.p.m. (d x q)	$^2J(^{13}C_{eq}Fe^{15}N)$	3.5 Hz
$[Fe(^{12}CN_{ax})(^{13}CN_{eq})_4(^{15}NO)]^{-2}$			
($^{13}C_{eq}$)	+134.4 p.p.m. (d)	$^2J(^{13}C_{eq}Fe^{15}N)$	3.6 Hz
(^{15}N)	b		
$[Fe(^{13}CN)_5(^{15}NO_2)]^{-4}$			
($^{13}C_{ax}$)	+174.0 p.p.m. (p x d)	$^2J(^{13}C_{ax}Fe^{13}C_{eq})$	9.1 Hz
($^{13}C_{eq}$)	+176.7 p.p.m. (d x d)	$^2J(^{13}C_{ax}Fe^{15}N)$	5.4 Hz
(^{15}N)	+174.4 p.p.m. (d x p)	$^2J(^{13}C_{eq}Fe^{15}N)$	1.9 Hz
$[Fe(^{13}CN_{ax})(^{12}CN_{eq})(^{13}CN_{eq})_3(^{15}NO_2)]^{-4}$			
($^{13}C_{ax}$)	+174.2 p.p.m. (q x d)	$^2J(^{13}C_{ax}Fe^{13}C_{eq})$	9.1 Hz
($^{13}C_{eq}$)	b	$^2J(^{13}C_{ax}Fe^{15}N)$	5.4 Hz
(^{15}N)	b	$^2J(^{13}C_{eq}Fe^{15}N)$	b
$[Fe(^{12}CN_{ax})(^{13}CN_{eq})_4(^{15}NO_2)]^{-4}$			
($^{13}C_{eq}$)	+176.7 p.p.m. (d)	$^2J(^{13}C_{eq}Fe^{15}N)$	1.9 Hz
(^{15}N)	b	$^2J(^{13}C_{eq}Fe^{15}N)$	b

a Chemical shifts measured in aqueous solutions referenced against external Me_4Si (^{13}C) or $CH_3{}^{15}NO_2$ (^{15}N); coupling: d=doublet, q=quartet, p=quintet.

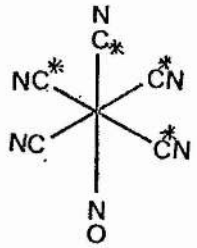
b Not observed.

3.2 Results.

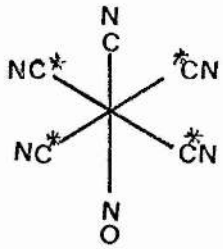
As part of a current line of investigation in this laboratory into sodium nitroprusside ($[Fe(CN)_5(NO)]Na_2$) and related species the ^{15}N and ^{13}C n.m.r. spectra were recorded for $[Fe(^{13}CN)_5(^{15}NO)]^{-2}$ and $[Fe(^{13}CN)_5(^{15}NO_2)]^{-4}$ (table 1). The crystal structure of $[Fe(CN)_5(NO)]^{-2}$ has been determined[2] and reveals that the ion has C_{4v} symmetry, with one axial and four equivalent equatorial cyanide ligands. The anion was prepared in this study by application of 90% enriched $Na[^{13}CN]$, resulting in a statistical distribution between the two sites, with 59.0% of the ions $[Fe(^{13}CN)_5NO]^{-2}$ (1), 26.2% $[Fe(^{13}CN_{ax})(^{12}CN_{eq})(^{13}CN_{eq})_3NO]^{-2}$(2) and 6.6% $[Fe(^{12}CN_{ax})(^{13}CN_{eq})_4NO]^{-2}$ (3). No other statistical combination of ^{12}CN and ^{13}CN represents more than 2.9% of the ions, too low for detection in this n.m.r. study.



(1)



(2)



(3)

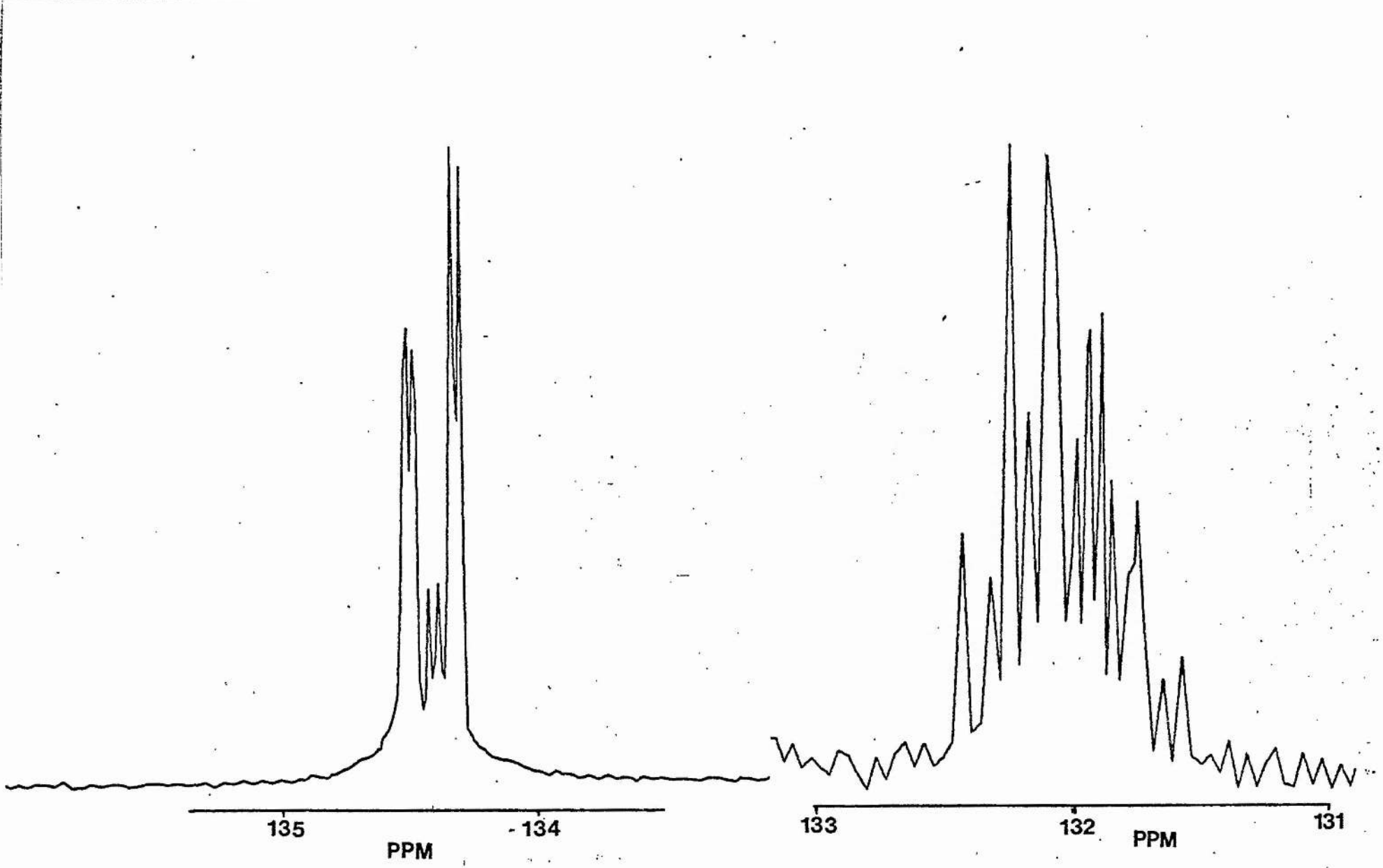


Fig. 1: ^{13}C n.m.r. spectrum of $[Fe(CN)_5(NO)]^{-2}$

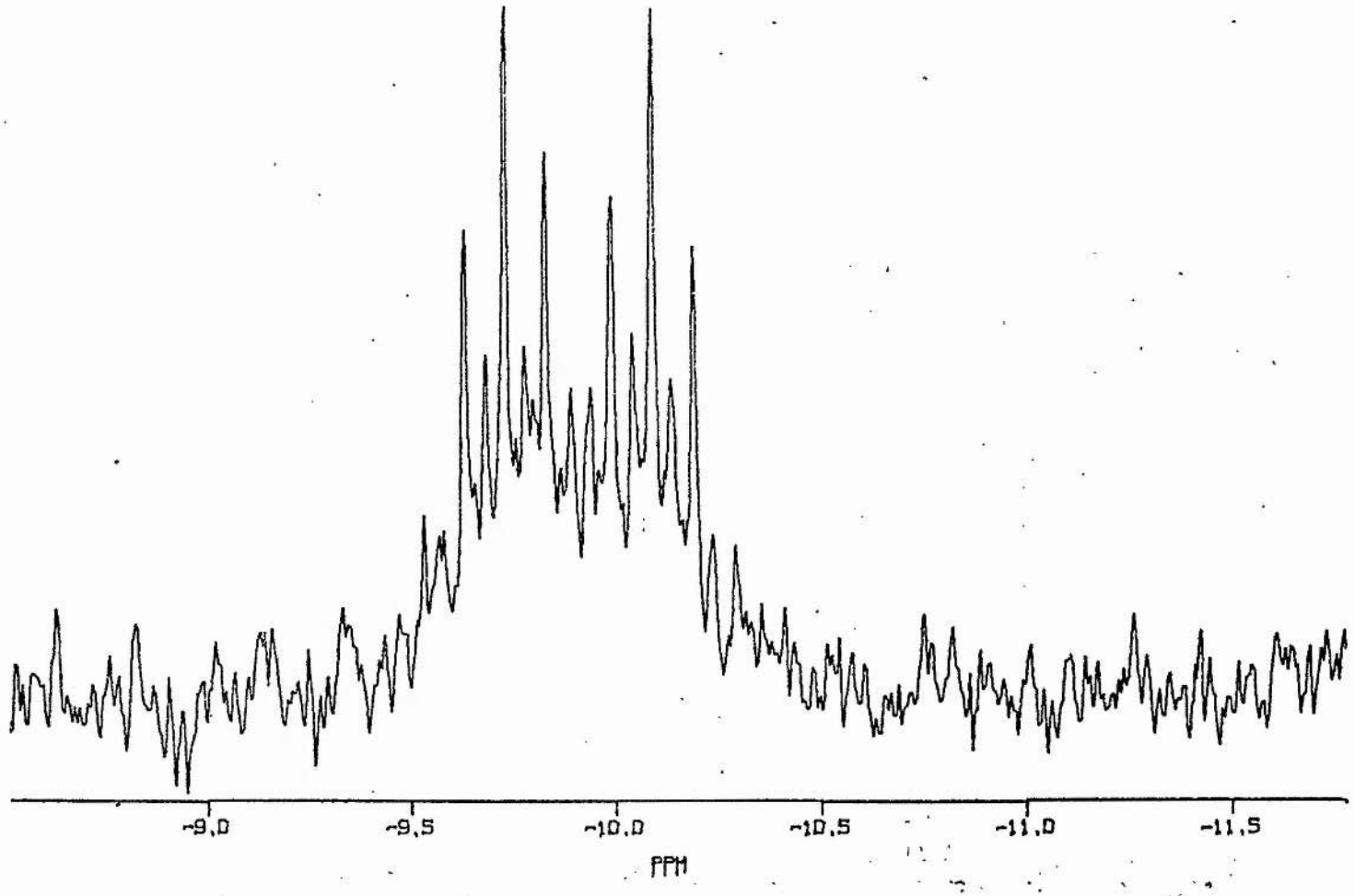


Fig. 2: ^{15}N n.m.r. spectrum of $[Fe(CN)_5(NO)]^{-2}$

In complex (1) there are two ^{13}CN environments in a 4:1 ratio. In complex (2) there are two environments in the ratio 3:1, and in (3) there is but a single ^{13}CN environment. The ^{13}CN n.m.r. spectrum of this enriched ion has been previously recorded by McGinnis[1,3]. The resulting spectrum possesses two ^{13}CN resonances in the ratio 4:1 (ca. 134.4 and 132.4 p.p.m.) due to the equatorial and axial cyanide ligands. In addition coupling is present to the other ^{13}CN ligands. In the equatorial ^{13}CN region (134.4 p.p.m.) a doublet is present due to (1) (resulting from the coupling of the axial ^{13}CN ligand (I=1/2)) and a singlet due to (3). In the axial region (132.2 p.p.m.) a quintet is present due to (1) (resulting from the coupling of four equivalent ^{13}CN ligands) and a quartet due to (2) (from the coupling of three equivalent ^{13}CN ligands).

Addition of $^{15}NO_2^-$ to aqueous $[Fe(^{13}CN)_5(^{14}NO)]^{-2}$ revealed that the nitrosyl group was labile to exchange. The ^{13}C n.m.r. of the mixture being essentially identical to that recorded for $[Fe(^{13}CN)_5(^{14}NO)]^{-2}$ except that additional coupling to a single ^{15}N (I=1/2) was resolved (fig. 1). The ^{15}N n.m.r. was recorded of the resulting ion (fig. 2), the spectrum being composed of an overlapping doublet of quintets and a doublet of qaurtets, due to (1) and (2). Due to the lower concentration of (3) and the larger line widths no coupling was observed which could be assigned unambiguously to this isomer.

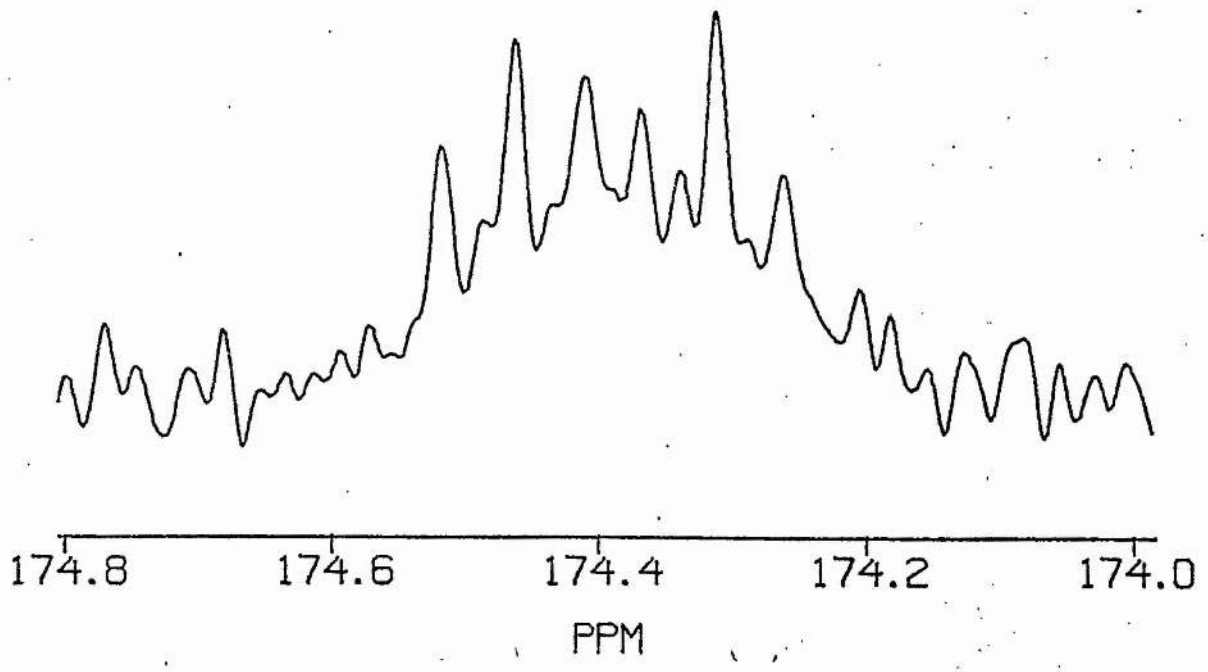


Fig. 3: ^{15}N n.m.r. spectrum of $[Fe(CN)_5(NO_2)]^{-4}$

$[Fe(CN)_5NO]^{-2}$ is readily converted to $[Fe(CN)_5(NO)_2]^{-4}$ by addition of base to aqueous solutions[4]. Addition of base to solutions containing $[Fe(^{13}CN)_5(NO)]^{-2}$ resulted in the generation of a new spectrum. This spectrum was similar to that of $[Fe(CN)_5(NO)]^{-2}$, except the absorptions were to low field of those assigned to $[Fe(^{13}CN)_5(NO)]^{-2}$ (174.0 and 176.7 p.p.m.). This new spectrum was assigned to $[Fe(CN)_5(NO_2)]^{-4}$, the assignment being confirmed by addition of base to solutions containing $[Fe(^{13}CN)_5(^{15}NO)]^{-2}$ by the increase in the multiplicity due to coupling to ^{15}N in the ^{13}C n.m.r. spectrum. Examination of the ion by ^{15}N n.m.r. yielded a spectrum (fig.3) essentially identical to that of $[Fe(^{13}CN)_5(^{15}NO)]^{-2}$ except that the chemical shift had moved to low field.

The nitrito complex $[Fe(CN)_5(NO_2)]^{-4}$, exists in an equilibrium with $[Fe(CN)_5OH_2]^{-3}$ [4]. Attempts to generate this species by addition of a large excess of base resulted in the observation of a weak spectrum which may have been the aqua complex ($^{13}C_{ax}$), 177.2 p.p.m.; ($^{13}C_{eq}$), 172.8 p.p.m., $^2J(^{13}C_{ax}Fe^{13}C_{eq})$, 9 Hz.

The Fe-N-O bond in $[Fe(CN)_5NO]^{-2}$ is an example of a linear nitrosyl, and the recorded ^{15}N chemical shift *ca.* -9.9 p.p.m. is within the range proposed by Mingos and coworkers[5-7] for such fragments. Few examples are recorded in the literature of metal nitrosyl fragments, even less are recorded for nitrito complexes and at present no comment can be made on a comparable range of ^{15}N nitrito frequencies.

3.3 References.

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